Modelling of simultaneously obtained small and wide angle synchrotron-radiation scattering depth profiles of ordered titania nanotube thin films

Krunoslav Juraić a, *, Milivoj Plodinec a, Irena Kereković b, Daniel Meljanac a, Vilko Mandić c, Davor Gracin a, Vesna Janicki a, Sigrid Bernstorf d, Miran Ćeh e, Aden Hodzic f, Andreja Gajović a

a Ruđer Bošković Institute, Bijenička cesta 54, Zagreb, Croatia
b University of Applied Health Sciences, Minarska cesta 38, 10000, Zagreb, Croatia
c Faculty of Chemical Engineering and Technology, Marulidžes trg 19, Zagreb, Croatia
d Sincrotrone Trieste, Strada Statale 14, km 163.5, 34149, Basovizza, TS, Italy
e Josef Stefan Institute, Ljubljana, Jamova 11, Slovenia
f Central European Research Infrastructure Consortium, Strada Statale 14, km 163.5, 34149, Basovizza, TS, Italy

A R T I C L E   I N F O

Keywords:
- Nanotube array
- Titanium dioxide
- GISAXS
- GIWAXS
- Anodization

A B S T R A C T

Thin films of vertically aligned titanium dioxide nanotubes are key constituents of charge transfer layers in 3rd generation photovoltaics. The beneficial charge transport primarily occurs due to the favourable microstructural features, i.e. the large effective surface-to-volume ratio. Here measuring methods are selected which are sensitive to microstructural features: Simultaneous Grazing Incidence Small and Wide Angle X-Ray Scattering (GISWAXS) and Scanning Electron Microscopy (SEM). Further, a model is developed for the simulation and explanation of the GISWAXS experimental data. Titanium nanotube arrays were investigated, which were previously successfully produced by electrochemical anodization of titanium thin film evaporated onto a zinc oxide coated glass substrate. The developed model was shown to be appropriate to describe the obtained samples, which consist of arrays of single nanotubes with a diameter of 40–80 nm, and a titanium dioxide layer with a porosity of 30–50%.

Within this work, we presented simultaneous GISWAXS as a comparable tool to SEM for the fast and successful study of the average nanotubes’ diameters in nanotubes arrays.

1. Introduction

Titanium dioxide (TiO₂) is one of the most intensively investigated compounds in material science due to its favourable essential properties. It is a wide band gap semiconductor having band-edge positions appropriate for solar cell applications and for hydrogen generation by water splitting [1, 2]. It is also known as a non-toxic, environment-friendly and corrosion-resistant material. Nano-forms of TiO₂ such as nanoparticles, nanorods, nanowires and, in particular, nanotubes can be used as photo-electrodes in dye-sensitized solar cells [3, 4]. The conversion efficiency of solar cells can be significantly improved by using oriented nanorod-like materials on top of a transparent conductive oxide [5].

Vertically aligned TiO₂ nanotube arrays can be prepared by electrochemical anodization of titanium foil in a fluoride electrolyte. Over the last decade, significant progress has been made in this field, particularly to obtain and to optimize the morphology of highly ordered TiO₂ nanotube arrays [6–8]. In this work, instead of using a several hundred microns-thick titanium foil as substrate for anodization, titanium thin films were used deposited directly onto transparent conductive oxide (TCO) coated glass substrates. The successful preparation of nanotube arrays in the form of transparent thin films on TCO/glass provides the opportunity for their application in thin films solar cells (perovskite or dye-sensitized). In addition, the same experimental procedure can be used for a straightforward preparation of such arrays on various other substrates, which could be beneficial in a range of applications.

Microscopic techniques like scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) are usually used for structural composition and surface morphology analysis of such samples. While SEM and HRTEM yield information about materials in direct space (which can be easily analysed), there are complementary techniques such as X-ray diffraction and scattering techniques which give information in the reciprocal space. Among this, grazing incidence X-ray diffraction (GIXRD) and small angle X-ray scattering (GISAXS) are particularly suitable for thin film sample analysis. These grazing incidence techniques are relatively new and
therefore there are only a few publications related to the investigation of ordered nanotube array samples performed by GISAXS. In this sense, Neelima [9] recently compared GISAXS and neutron scattering results obtained from titania nanotubes arrays.

GISWAXS is an experimental technique which gives insight into the material crystal structure (GIWAXS) and the surface layers morphology on the nanometer scale (GISAXS). The use of synchrotron X-ray radiation (high flux, brilliance and stability) allows to perform GISWAXS even on very thin films or small sample volumes, and on very weakly scattering materials. Two main advantages of GISWAXS over microscopy are, that data are obtained averaged over a “large area” (several square millimetres), and that simultaneously information can be obtained about the crystal structure and surface morphology on the nanometer scale. By varying the grazing incidence angle, the penetration depth of the probing X-ray beam can be changed from the surface layer towards the bulk of the sample, which enables to perform a depth-dependent analysis across the sample. When comparing SEM and GISAXS, the main disadvantage of the latter one is the need for a proper computational model that for analysis the data interpretation proper fitting models for the experimental data are needed and this work is, in its most important part, a contribution to overcoming this problem.

Recently the preparation of TiO₂ nanotube array thin films and the influence of the Ti substrate morphology on the nanotubes’ growth has been reported [10]. In this work, the focus lies on the quantitative analysis of the nanotubes dimensions (inner radius and wall thickness) obtained by GISWAXS. Most part of this work is devoted to developing an appropriate way for the analysis of the GISAXS data for the actual case, nanotube arrays. A model is outlined for the analysis of GISAXS intensity pattern obtained on such samples, which is based on the Distorted-Wave Born Approximation (DWBA) [11] assuming a form factor of vertically aligned core-shell cylinders and including the corrections for the non-perfect geometry of the samples. The simulation results (the nanotubes inner and outer diameter distributions) are then compared with results obtained from SEM micrographs.

2. Experimental

2.1. Sample preparation

A 3-step process was used for the TiO₂ nanotube array thin film samples preparation. In the first step titanium layer was deposited on magnetron sputtered Al-doped zinc-oxide covered glass substrates 20 x 20 mm in size (Fig. 1a). Prior to the Ti layer deposition, the ZnO-glass substrates were cleaned using the standard procedure in an ultrasonic bath: first 10 min in acetone, then 10 min in ethanol and 10 min in Milli-Q water. Finally, the substrates were dried under flowing nitrogen. The substrates were preheated to 230°C and electron beam evaporation was used for the Ti layer deposition (Fig. 1b). The starting material was 99.9% Ti 0.2–1.5 mm granulate from Balzers. The thickness of the deposited Ti layer (1.2 μm) was monitored in situ by a quartz crystal microbalance monitor. It is not expected that during this deposition the substrate temperature significantly exceeded 100°C.

In the second step, the Ti layers were anodized in the shape of the circular area having 8 mm in diameter (Fig. 1c) and TiO₂ NTs were formed in that part of Ti layer as is shown in the schematic view of all the layers in cross section (Fig. 1d). For the anodization at room temperature, a conventional two-electrode system was used with a Pt foil as the counter electrode and a Ti layer as the anode [12]. The diameter of the circular etched area was 10 mm. Ethylene glycol containing 0.3 wt% of NH₄F and 2 vol% of distilled water was used as electrolyte [12]. The DC voltage for anodization was varied in the range 40–60 V in order to obtain samples with various nanotube diameter. Since for photovoltaic use, the transparent TiO₂ layer is favourable, the anodization time (30–75 min) was adjusted to etch the titanium layer as much as possible and thus to obtain a transparent TiO₂ NT layer (Table 1).

![Figure 1](https://example.com/fig1.png)

**Table 1** Parameters used in anodization process: applied voltage and duration of anodization and results of SEM images analysis: average inner and outer nanotubes radius.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anodization voltage [V]</th>
<th>Anodization time [min]</th>
<th>SEM R&lt;sub&gt;i&lt;/sub&gt; [nm]</th>
<th>SEM R&lt;sub&gt;out&lt;/sub&gt; [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT-60V-60m</td>
<td>60</td>
<td>60</td>
<td>18.0 ± 2.3</td>
<td>48.4 ± 5.3</td>
</tr>
<tr>
<td>NT-50V-30m</td>
<td>50</td>
<td>30</td>
<td>11.0 ± 0.9</td>
<td>29.9 ± 3.0</td>
</tr>
<tr>
<td>NT-40V-75m</td>
<td>40</td>
<td>75</td>
<td>8.6 ± 1.9</td>
<td>33.3 ± 4.5</td>
</tr>
<tr>
<td>NT-40V-45m</td>
<td>40</td>
<td>45</td>
<td>10.1 ± 1.6</td>
<td>41.9 ± 3.8</td>
</tr>
<tr>
<td>NT-40V-30m</td>
<td>40</td>
<td>30</td>
<td>9.8 ± 1.8</td>
<td>35.3 ± 4.3</td>
</tr>
</tbody>
</table>

For samples anodized at 40V, anodization time was varied to obtain layers with different nanotube length.

During the anodization, the applied voltage was kept constant, and the current was monitored by a Fluke 17B multimeter. A typical current variation over time is presented in Fig. 2, so from that variation the phases of NT formation can be recognized. Thus, during the first minute, the current decreases rapidly (phase I), which corresponds to the formation of a compact oxide layer on the electrolyte/Ti interface. Then during the next 3–4 min current starts to decrease much slower (phase II), that represent the start of nanotubes formation within the Ti. This effect is much more pronounced (with additional plateau) for titanium foil anodization and corresponds to the formation of the porous structure [13]. After that follows a gradual current decrease (phase III) indicating that the formation of pores reach equilibrium with the dissolution, that phase persist up to moment when the titanium layer is completely etched (the electrolyte comes in direct contact with the ZnO coated glass substrate). At that moment the current starts to increase rapidly. This moment is not presented in Fig. 2, since
the anodization process should be stopped earlier to avoid short circuit in the case of using the prepared materials as electrode transporting layer in dye or perovskite photovoltaics.

After anodization, the formed TiO₂ NT array samples were washed in distilled water and dried by compressed air.

In the third step, the TiO₂ NT array samples were calcined in an oven at 450°C for 1h in the air atmosphere (heating rate 5°C/min) in order to obtain Ti anatase phase.

2.2. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS)

The surface morphology and chemical analyses of the sample were obtained with a field-emission gun (FEG) scanning electron microscope (JEOL JSM-7610F). The imaging was performed at 10 kV accelerating voltage and a working distance of 8 mm with the SEI detector configuration. For energy-dispersive X-ray spectroscopy (EDXS), INCA Oxford 350 EDS SDD was used. Spectra were recorded at 15 kV accelerating voltage and 15 mm working distance.

Several SEM images obtained at higher magnification (X 100k) were used for the quantitative analysis. Using the ImageJ software, the areas of each nanotube (inner and outer) were marked. The diameters of each marked nanotube were calculated from the obtained areas assuming that the nanotubes have a perfect circular cross-section.

2.3. Grazing incidence small- and wide-angle X-Ray scattering (GISWAXS)

Simultaneous GISWAXS experiments were performed at the Austrian SAXS beamline at the Elettra synchrotron radiation center in Trieste (Italy) using an 8keV X-ray beam [14]. The beam size at the sample position was HxV = 0.2 mm × 1 mm (H = normal to sample surface, V = parallel to sample surface). This beam size was optimized in order to increase the resolution in the direction parallel to the sample surface but at the same time to keep an acceptable signal to noise ratio. For the GISAXS experiment, a Pilatus 1M detector (981 × 1043 pixels and 172 × 172 μm² pixel size) was positioned in the plane normal to the X-ray beam and at a distance of 1976 mm from the sample. The samples were measured in air, but a vacuum chamber was used in the space between the sample stage and the GISAXS detector to minimize air scattering. The angular positions of the pixels in the GISAXS images were calibrated with the silver behenate powder standard.

The GIWAXS detector (Pilatus 100K, 487 × 195 pixels, 172 × 172 μm² pixel size) was positioned very close to the sample at a distance of 177.8 mm and with a detector to sample surface tilt of 55° (Fig. 3).

LaB₆ powder (from NIST) in a capillary was used for the GIWAXS angular scale calibration.

The angle of grazing incidence was varied starting from the critical angle αc for total external reflection for the porous TiO₂ NT array and increased in small steps until the TiO₂-ZnO interface was reached (αc = 0.2°, αc + 0.3°, and αc + 1.0°). The corresponding penetration depth values (calculated using equation A8 in Appendix 4) were determined using equation A8 in Appendix 4 and are: 10 nm, 25 nm, 165 nm, 270 nm, 400 nm. The precise values for the grazing incidence angles and especially the critical angle for total external reflection were determined from 1D cuts taken in the specular plane from 2D GISAXS intensity patterns (Q₀ = 0) detecting the positions of the maximum of the directly reflected beam and the Yoneda maximum.

3. Results and discussion

3.1. SEM and EDXS results

The surface of the Ti substrate, deposited by electron beam evaporation on ZnO coated glass and used as the starting layer for anodization, consists of 100–200 nm large grains. The 30° tilted SEM image indicates that the larger grains are agglomerates of smaller nanocrystals (Fig. 4f).

The parameters of the anodization process (applied voltage and electrolyte content) were optimized to obtain highly ordered vertically aligned TiO₂ nanotube array samples (Fig. 4).

The averaged single nanotube outer diameter measured in SEM images was in the range 60–100 nm and the inner diameter in range 15–40 nm (Table 1). Since the outer diameter of the obtained nanotubes was 3–4 times larger than inner, therefore nanotubes have 22–30 nm thick walls. Usually, obtained wall thickness is much smaller for nanotubes formed by using Ti foil for anodization as was the case in our previous studies [12,15]. From Fig. 5 can be recognized three different classes of samples: 1) samples with very densely packed touching nanotubes (Figs. 5a), 2) samples with almost completely separated nanotubes (Figs. 5b) and 3) samples with nanotubes organized in larger or smaller clusters (Fig. 5c). With the aim to show how the height of the nanotubes varied with anodization time, SEM images of the vertical side of the nanotubes are shown in Fig. 5. Height of prepared TiO₂ thin films can be estimated from Fig. 5 where are presented images for samples prepared using identical voltage (40 V), while anodization time is varied (30, 45, and 75 min). Height of the nanotubes obtained after 30 min of anodization was approximately 500 nm, the nanotubes after 45 min was 800 nm, while after 75 min of anodization the height was 1200 nm.

EDXS spectra obtained at every sample were similar, therefore only one representative EDXS are shown in Fig. 6. The spectrum confirms the sample content: the Ti and O elements are in the nanotube layer, Zn, Al and O in the Al-doped ZnO transparent conductive layer and...
Si in the glass substrate. The EDXS, shown in Fig. 6b, was taken from the sample area presented in the SEM image of Fig. 6a. The small amount of carbon is related to surface layer contamination.

3.2. GIWAXS results

2D GIWAXS patterns (Fig. 7) were reduced to the standard 1D diffraction pattern using the Nika Igor Pro package [16].

The GIWAXS data were used only for qualitative analysis because there is a significant contribution of the instrumental profile to the diffraction peaks broadening due to the used grazing incidence geometry. This is due to the facts that the incident X-ray beam has a very long footprint on the sample surface, and a 2D planar detector (placed close to sample stage) was used for GIWAXS signal detection instead of a point or curved detector. For example, for a grazing angle of incidence of 0.5° and a beam width of 0.2 mm in the direction perpendicular to sample surface, the beam footprint on the sample surface is 23 mm long. Diffraction peak width is highly dependent on sample size. Also, diffraction peak positions are dependent on sample position at the sample stage. This fact can explain small shifts of diffraction peaks from values taken from literature.

Fig. 8 show GIWAXS 1D diffraction patterns for all the studied samples compared to ZnO coated glass substrate and Ti layer used for anodization. Ti layer, as-deposited onto ZnO coated glass substrate is completely amorphous (broad peak between 30° and 45°). After anodization samples are still amorphous (60V, 60 m n.a.), but after the calcination process, the TiO₂ anatase phase is formed (appearance of a diffraction peaks characteristic for the anatase phase (101) peak at 25° and other less prominent peaks).

3.3. GISAXS results

In Fig. 9 are presented illustration of GISAXS 2D images for as-deposited Ti substrate (a and b) and TiO₂ NT samples after anodization (c and d). Figures a) and c) are taken for the angle of incidence equal to the critical angle for total external reflection for Ti and TiO₂ NT
contains information only about sample surface morphology (Fig. 9a and c). For higher values of angle of incidence (Fig. 9b and d) beam penetrate much deeper below sample surface and provide information from larger volume below the sample surface.

For the Ti substrate sample (9a), which has a flat surface, the GISAXS maximum is well defined with wide Yoneda wings in the direction parallel to sample surface [17]. Diffuse scattering is concentrated close to specular plane (Q_y = 0 nm⁻¹), at the Yoneda maximum line (Q_y = const.) a broad maximum can be observed at the position Q_y = 0.75 nm⁻¹ which corresponds to objects 7-10 nm in size and can be related to Ti nanocrystals observed also in SEM images (Fig. 4f). As-deposited Ti samples are homogenous in depth and there is no additional contribution to GISAXS signal for larger value of angle of incidence.

For anodized samples, the GISAXS images (c and d) consists of the intensity contribution from the Ti substrate and the anodized circular area (TiO₂ NT array) because the incident X-ray beam footprint on the sample surface is very low. Position of Yoneda maxima for Ti (Fig. 9a) is positioned at significantly higher Q_y value then for TiO₂ NT sample (Fig. 9c). This is a direct consequence of high porosity (lower electron density) of TiO₂ NT sample.

For quantitative analysis 1D cuts are done in direction normal to sample surface (Q_y = const.) and direction parallel to sample surface (Q_z = const.).

Intensity cuts normal to the sample surface (Q_z = const.) close to the specular plane (Q_z = 0) and outside of the beam-stop area, are used for critical angle determination (Fig. 10). Two Yoneda maxima are observed for TiO₂ NT sample (Figs. 9d and 10b). The lower one is related to the NT etched area and the higher one to the ZnO substrate or Ti surrounding.

The position of the Yoneda maxima and the specular (directly reflected) maxima were used for the index of refraction calculation and the density estimation [18]:

\[ \theta_{\text{Yoneda}} = \alpha_0 + \alpha_c \]

\[ \alpha_c = \sqrt{2\delta} \]

\[ \delta = \frac{r_d^2 \lambda^2 \rho_e}{2} \]

where \( \alpha_0 \) is the angle of grazing incidence, \( \alpha_c \) is the critical angle for total external reflection and \( \delta \) is the real part of the index of refraction \( n = 1 - \delta + i\beta \), \( r_d \) is the classical radius of the electron, \( \lambda \) the wavelength and \( \rho_e \) the electron density.

In Fig. 11 are compared 1D cuts in the direction normal to the sample surface slightly outside the beamstop region (Q_y = -0.144 nm⁻¹) in order to avoid the beamstop area where the scattered intensity is attenuated. The sample with TiO₂ nanotubes surrounded by substrate area shows two Yoneda maxima (critical angles for total external reflection) corresponding to two materials with different electron densities. The lower critical angle \( \alpha_C = 0.174° \) corresponds to the porous TiO₂ NT material and the higher one \( \alpha_C = 0.288° \) corresponds to the surrounding compact dense Ti area. This value is in rather good agreement with the theoretically calculated values for Ti bulk material (\( \rho = 4.54 \) g cm⁻³) \( \alpha_C = 0.299° \) and TiO₂ bulk material (\( \rho = 4.26 \) g cm⁻³) \( \alpha_C = 0.295° \). Some lower values of \( \alpha_0 \) than theoretical values obtained for Ti can be explained by oxidation of Ti surface.

For the lowest used grazing angle of incidence, only one Yoneda maximum can be observed because that angle of grazing incidence is lower than the critical angle for titanium (Fig. 10b). The region around the Yoneda maxima was fitted to the well-known equation including the Fresnel transmission coefficients, and the critical angle was calculated (Eq. A6 in appendix).

The obtained critical angle for total external reflection from the TiO₂ nanotube array is much lower than the characteristic...
values for Ti and TiO2 bulk material. The reason is that the effective density of the TiO2 nanotube array samples is decreased due to the empty spaces between and inside the single tubes.

The porosity was calculated from the ratio of the critical angles for total external reflection for bulk TiO2 material and the TiO2 nanotube array layer using the equation [19]:

\[ P = \frac{\rho_{\text{bulk}} - \rho_{\text{nanotubes}}}{\rho_{\text{bulk}}} = 1 - \frac{\rho_{\text{nanotubes}}}{\rho_{\text{bulk}}} = 1 - \left(\frac{\sigma_{\text{nanotubes}}}{\sigma_{\text{bulk}}}\right)^2 \]

(4)

The obtained porosity values were in the range 30-40% for all analysed samples.

For the anodized samples, 1D cuts taken parallel to the sample surface at the Yoneda maximum position show maxima related to the ordered array of nanotubes produced by anodization (Fig. 11).

The Yoneda maximum vanishes for the angle of grazing incidence significantly larger than the critical angle for total external reflection (Fig. 9d). A larger angle of incidence means a larger penetration depth below the sample surface and thus an additional GISAXS scattering contribution from the bottom part of the nanotubes which is not perfectly arranged with the top part.

1D cuts in the direction parallel to sample surface at the position of Yoneda maximum are used for quantitative analysis of nanotubes lateral dimensions (inner and outer diameter). In Fig. 11 are presented 1D cuts for selected TiO2 NT samples prepared using different anodization voltage. Position of observed peaks is related to nanotubes dimensions. Peaks are very weak because of variation in nanotube diameter, wall thickness and nanotube inclination (presented Fig. 5, SEM side view). For a higher angle of incidence, peaks are not anymore observed because larger sample volume below the sample surface contribute to GISAXS signal and variation in nanotubes diameter and inclination are more pronounced.

To simulate GISAXS pattern from TiO2 nanotube array samples a theoretical model was made in the framework of the Distorted Wave Born Approximation (Eq. (A4) in the Appendix). This model is based on 1μm long vertically aligned core-shell cylinders (Eq (A3), A1 in the Appendix). The inner empty cylinder and the shell with a refractive index of equal to that from bulk TiO2 were obtained from Ref. [20].

A Gaussian distribution was used for the description of the inner cylinder diameter and the shell thickness with two free parameters: mean value and standard deviation (Eq (A5) in Appendix).

The calculations were done using the BornAgain software [21] with a custom-written python script. A rectangular detector with correction for the finite pixel size of the Pilatus detector was used in the calculations. Four parameters were selected for variation and optimization: mean value and standard deviation for the inner cylinder radius, and mean value and standard deviation for the shell thickness.

During the numerical calculation ensembles of 50–100 nanotubes with different inner radii and shell thicknesses were generated by using bivariate Gaussian distributions. The Gaussian distribution parameters selection was restricted to an interval ±2σ around the mean value.

To avoid time-consuming numerical calculations during the 1D cuts simulation a variation of the nanotubes length and inclination was neglected. Examples of fits obtained in that way are shown in Fig. 11.

The values for the inner and outer radii obtained from the GISAXS experiments are in good agreement with the SEM results (Fig. 12). However, GISAXS gives systematically larger values for the outer nanotube radius. Side view of nanotubes (Fig. 5) shows that nanotubes have a smaller diameter at the top (close to sample surface) which is seen by SEM. Opposite to that, GISAXS gives information averaged over larger volume below sample surface (depending on the angle of incidence) where nanotube diameter is increased.

4. Conclusion

Vertically aligned TiO2 nanotube arrays were successfully prepared by anodization of electron beam evaporated titanium thin films. SEM and simultaneous GISAXS were applied for the structural analysis. It was shown that ordered vertically aligned nanotube arrays could be obtained, with single nanotube outer diameters in the range of 50–100 nm, inner diameters of 15–40 nm and an average layer porosity of 30–40%. A model was developed for the simulation of the GISAXS pattern obtained from TiO2 nanotubes arrays. The simulation results are in good agreement with SEM data which verifies the way of analysis.
Fig. 9. 2D GISAXS images from the Ti coated ZnO-glass substrate for angle of incidence (a) $\alpha_i = \alpha_c$ and (b) $\alpha_i = \alpha_c + 0.3^\circ$, and from the TiO$_2$ nanotube array sample (NT-60V-60m) for angle of incidence (c) $\alpha_i = \alpha_c$ and (d) $\alpha_i = \alpha_c + 0.3^\circ$.

Fig. 10. Comparison of 1D cuts taken normal to the sample surface for (a) Ti substrate and (b) TiO$_2$ NT array measured at the critical angle and angles slightly higher than the critical angle. The position of Yoneda maxima for the Ti surrounding and TiO$_2$ nanotubes are annotated by arrows.
The core shell (hollow) particle (shape) form factor is calculated as [22]:

$$F_{cs}(\mathbf{q}) = F_{co} + \tau \left(F_{sh} - F_{co}\right)$$

(A3)

where $F_{co}$ is the form factor of the inner cylinder with radius $R_{\text{inn}}$ and index of refraction $n_{co}$ (in our calculations equal to 1), $F_{sh}$ is the form factor of the outer cylinder with radius $R_{\text{out}}$ and index of refraction $n_{sh}$ (in our case the value for bulk TiO$_2$), and $	au$ is a correction factor.

Calculations are done in the framework of the Distorted Wave Born Approximation (DWBA). In the DWBA the particle form factor is calculated as the sum of four terms involved in the scattering process associated to different scattering events [22]:

$$F_{tot}(q_x, q_y) = F(q_x, q_y) + F(q_x, q_y) + F(q_x, q_y) + F(q_x, q_y)$$

where $q_x$ and $q_y$ are the $x$ and $y$ components (normal to the sample surface) of the incident and scattered wave vectors, $R_p$ is the Fresnel refraction factor, $\alpha_i$ the angle of grazing incidence, $\alpha_f$ the scattering angle. The total form factor is calculated as 2D integral of the core-shell cylinder form factors with normal distributed inner radius and shell thickness $(d_{\text{shell}} = R_{\text{out}} - R_{\text{in}})$. To calculate a 2D integral it is generated a 2D equally distributed grid in intervals ($-2\sigma_{d_{\text{shell}}}, 2\sigma_{d_{\text{shell}}}$). For each mesh in the grid is calculated a weighting factor for the form factor scaling as bivariate normal distribution:

$$W(R_p, d_{\text{shell}}) = \frac{1}{2\pi \sigma_{R_p} \sigma_{d_{\text{shell}}}} e^{-\frac{1}{2} \left(\frac{R_p - R_{\text{in}}}{\sigma_{R_p}}\right)^2 + \frac{d_{\text{shell}}^2}{\sigma_{d_{\text{shell}}^2}}}$$

(A5)

where $R_{\text{in}}, \sigma_{R_p}, \sigma_{d_{\text{shell}}}$ are parameters (mean value and standard deviation) of the inner radius and shell thickness normal distribution.

The scattered intensity below and around the Yoneda maximum can be described by:

$$I(\mathbf{q}) = A \left| t(\mathbf{k}_i) t(\mathbf{k}_f) \right|^2 F(q)$$

(A6)

where $A$ is constant, $F(q)$ is the form factor, and $t(\mathbf{k}_i)$ and $t(\mathbf{k}_f)$ are Fresnel factors for the refraction of the incident and scattered wave vectors:

$$t = \frac{2k_z}{k_{iz} + k_{zf}} = \frac{2 \sin \alpha_i}{\sin \alpha_i + \sqrt{n^2 - \cos^2 \alpha_i}}$$

(A7)

where $\alpha_i$ is the angle of incidence and $n$ is the complex index of refraction.

X-ray attenuation length $\Lambda$ is defined as the depth into the material measured along the surface normal where the intensity of x-rays falls to 1/e of its value at the surface [23]:

$$\Lambda = \frac{\lambda}{2V/2\pi} \left\{ \sqrt{\left(\alpha_i^2 - \alpha^2\right)^2 + 4\beta^2 - \alpha_i^2 + \alpha^2} \right\}^{-1}$$

(A8)

where $\alpha_i$ is the angle of grazing incidence, $\alpha_c$ is the critical angle for total external reflection and $\beta$ is the imaginary part of the index of refraction $n = 1 - \beta + i\delta$ and $\lambda$ the wavelength.

References
