Nanoscale investigation on large crystallites in TiO₂ nanotube arrays and implications for high-quality hybrid photodiodes

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Abstract Anodized TiO₂ nanotube arrays fabricated on a TiO₂ thin film on conducting glass substrates can be readily implemented in diverse applications like hybrid solar cells. In this study, we concentrate on morphologies with inner tube diameter being around 30 nm which is in dimension of the exciton diffusion length of common organic hole conductors. Cross-sectional preparation of the intact tube array in correlation with transmission electron microscopy has been performed to get local information on the TiO₂ nanotubes and their arrangements, depending on anodization voltage. Crystallites have been found to be anatase and in size of several hundred nanometers along tube walls with increasing length for increasing anodization voltages. Inter-tube connections with similar crystal orientations of adjacent tubes are found. These give rise to large areas of uniform orientation. Thus, the number of grain boundaries within the film is low compared to the reported values for different TiO₂-polymer material systems. Using the arrays, hybrid TiO₂ solar cells were fabricated, which show high fill factors indicating good electron transport. The results suggest high electron mobility and are encouraging for a

utilization of the nanotube arrays in next generation photovoltaics.

Introduction

TiO₂ is a versatile metal oxide which has tunable optical and electronic properties depending on its different structures and can be produced by various fabrication routes. In recent years, several fields of application are more and more using nanostructured TiO₂, often to maximize surface areas and accordingly interface areas when combined with other materials [1]. A few very important examples are the anodized TiO₂ nanotube arrays, among others used in thin-film solar cells; [2–8], lithium-ion batteries [9]; hydrogen sensors [10, 11]; and water photolysis [12, 13]. A consequence of downsizing structures is the change in their physical and chemical properties, which again cause modification of important electronic properties, especially the mobility of electrons along and between tubes [1]. In this regard, electron trap states have been identified to be a limiting factor [14]. TiO₂ nanotube arrays have been analyzed via intensity-modulated photocurrent and intensity-modulated photovoltage spectroscopy, and the electrons' crossing at grain boundaries was found to be severely affected by these trap states. Hence, large crystallites along the tubes are surmised to facilitate excellent electron transport [15, 16].

The present study aims at an elucidation of the material properties of anodized nanotubes forming an array on conducting glass. A scheme of the studied layer system is shown in Fig. 1. As previously shown in a detailed scanning electron microscopy (SEM) study, dimensions of these nanotubular arrays can be directly controlled by adjusting the conditions of electrochemical anodization, in

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Fig. 1 Scheme of the sample. The nanotubes are composed of anatase, while the TiO_2 flat film has rutile structure. ITO was used as conducting glass (Color figure online)

particular, the anodization bath temperature and the anodization voltage [17]. Four different voltages (10, 15, 20, and 25 V) have been applied during fabrication. They were chosen to receive inner tube diameters of around 30 nm, which is in the order of dimension of the exciton diffusion length in semiconducting polymers like poly(3-hexylthiophene) (P3HT) [18], rendering them particularly interesting for applications in solid-state dye-sensitized hybrid solar cells. Since an anodization voltage of 10 V resulted in a partially dissolved array composed of damaged tubes, it is not studied further.

Up to now, SEM and X-ray diffraction (XRD) were used as standard analysis methods for TiO_2 nanotube arrays, while transmission electron microscopy (TEM) has been applied on single nanotubes or dissolved arrays [15, 19–21]. In this study, TEM has been chosen as primary method for analysis to gain local information about tube morphology, phase purity, crystal grain size, and crystal orientation within the tubes in context of the intact array. The results are correlated to properties by fabricating hybrid solar cells composed of the TiO_2 nanotube arrays, a common ruthenium dye and P3HT. This design is adequate to gain basic information while maintaining simplicity and comparability, so that results can be appraised in the context of already existing studies. Current–voltage measurements have been carried out to characterize electronic behavior, with a focus on the fill factor which is influenced by electron mobility and charge recombination.

Experimental section

TiO_2 nanotubes were synthesized on tin-doped indium oxide (ITO)-coated glass substrates. ITO substrates were successively cleaned in ultrasonic baths of acetone and isopropanol for 30 min each, dried in N_2 stream and subjected to a 7-min cleaning in an O_2 plasma. Substrates were transferred to the main chamber of a NanoSystems Gamma

1000C sputter system with a base pressure of 3×10^{-8} Torr. Approximately, 40 nm TiO_2 and 400 nm Ti were DC sputtered at 500 °C and Ar gas pressures of 5 and 4 m Torr, respectively. Samples were anodized in an ethylene glycol-based electrolyte containing 0.4 wt% NH_4F and 2 vol% deionized water. Anodizations were carried out in a two-electrode setup versus a Pt counter electrode at room temperature and different anodization voltages. Anodization was stopped after complete consumption of the Ti feed substrate, but before corrosion of the underlying ITO as described elsewhere [17]. After anodization, samples were excessively rinsed with EtOH, slowly dried in air and annealed on a hotplate at 450 °C in ambient air for 1 h with heating and cooling rates of 5 and 2.5 °C/min, respectively.

TEM cross-sectional specimens have been prepared via standard route by gluing a sandwich of the layers into a brass tube, cutting of slices, grinding, dimpling, and ion milling according to Strecker et al. [22]. For TEM investigation, a Jeol JEM 2011 operated at 200 kV and a FEI Titan (S)TEM 80–300 operated at 300 kV have been used. The Titan is equipped with an EDAX detector for energy dispersive X-ray analysis. Off-axis dark-field (DF) images have been taken without use of beam-tilting.

Hybrid solar cells were fabricated based on TiO_2 nanotube arrays anodized at 25 V as described above. The anodized and annealed nanotubes of 500–600 nm length were immersed for 18 h in a 0.4 mM ethanol solution of the ruthenium dye Z907 [23]. Subsequently, samples were rinsed with ethanol and dried in ambient air. P3HT was deposited on top of the nanostructures as hole conductor. It was prepared as a 30 mg/ml solution in chlorobenzene and spin coated at 1200 rpm for 1 min after leaving the solution on the substrate for 2 min to achieve sufficient wetting of the nanotubes. Immediately after spin coating, the films were annealed at 150 °C for 1 min in ambient air. Then, a ~50 nm thick layer of poly(3,4-ethylenedioxythiophene)–polystyrene sulfonic acid (PEDOT:PSS) was spray-deposited onto the P3HT as described previously [24]. In brief, PEDOT:PSS was diluted in 2-propanol at a ratio of 1:10 and the substrate was wetted with the solution via spraying. Subsequently, the film was spin coated at 800 rpm for 1 min. Solar cells were finalized by DC sputtering Ag top contacts through a shadow mask, resulting in an active area of 0.125 cm².

Solar cells were tested in the dark and under illumination with a LOT-Oriel LS0106 AM 1.5 g solar simulator. The light intensity was adjusted to 100 mW/cm² with a Fraunhofer Institute certified Si solar cell as a reference. Current density–voltage (I–V) characteristics were recorded using a Keithley Sourcemeter 2400 controlled by a self-written LabView program.

Results

Bright-field (BF) overview images were taken to get information about the tube length, ranging from 475 to 575 nm for increasing voltage (Fig. 2). The values are in accordance to the results from SEM analysis, which has been performed earlier, although the tube length at the 15 V sample is slightly larger than expected [17]. The increasing length at higher anodization voltages could be confirmed. Wall thicknesses have been measured in slightly higher magnified BF images (not shown) and result in averages of $9 (\pm 1)$, $9 (\pm 2)$ and $12 (\pm 2)$ nm for 15, 20 and 25 V anodization voltages, respectively. Owing to the sample thickness, pore diameters were hardly distinguishable, but exemplary areas showed inner diameters of around 30 nm for all anodization voltages with a slight tendency to increase at higher voltages. Energy dispersive X-ray analysis (not shown) exhibits that the tubes contain mainly titanium and oxygen, with some traces of sodium in all samples and calcium in the 15 V sample only, which are probably residues from the sample preparation.

For a better understanding of electronic behavior, further investigation of the crystalline structure and phases was performed. Electron diffraction (ED) patterns show polycrystalline anatase. At specific areas, DF images were taken to determine crystal sizes. Figure 3 shows BF images, their corresponding ED patterns and DF images. The ED patterns, which have been taken at circular areas of about 650 nm diameter, show distinguishable major reflections in all cases, contrary to ring-like structures which would have been expected for fully polycrystalline samples. In accordance, the DF images taken with the indicated (200), (101) and (101) reflections of anatase confirm that a large grain size along the tube wall and a similar orientation over several nanotubes is present. Thus,

although these areas show no single crystal, they appear to be composed of larger grains (including slight rotations) and some smaller grains filled in between.

The crystalline appearance along the tube walls is assumed to be one of the most important features allowing a high conductivity parallel to the tube axis. For the present samples, the results indicate that the grain size along this axis is several 100 nm for individual tubes. These large crystals can only be distinguished when they are oriented near a zone axis and were observed at various positions within the sample. Groups of nanotubes with similar crystal orientation extend up to 500 nm in diameter, like the one shown in Fig. 3c. Thus, adjacent tubes often appear with the same orientation.

BF images typically show Moiré patterns in wide areas, which indicate crystallites slightly rotated by few degrees against each other. Since reflections with nearly similar angle cannot be separated by the objective aperture in ED patterns, these overlapping grains contribute to DF images, resulting in Moiré patterns here as well. Owing to their appearance in clearly distinguishable nanotubes, like the one marked by an arrow in Fig. 3c, it is assumed that the crystals of the transmitted front and back tube walls are slightly rotated with respect to each other. In addition to these findings, a trend toward developing a larger grain size at higher anodization voltages is observable. The mean lengths of the 10 largest crystals found for each voltage are 210 nm (160–260 nm; 15 V), 260 nm (230–310 nm; 20 V), and 320 nm (250–360 nm; 25 V).

For establishing further proof of the large crystal size, series of HRTEM micrographs have been captured at various tubes. An exemplary one is given in Fig. 4. The left BF image shows large parts of a nanotube which has been cut at the top during ion milling. Its darker appearance hints at an orientation parallel to a zone axis. At the closed end just below box 4, Moiré patterns are visible again, and so nearly similar crystal orientations are present. Boxes numbered from 1 to 4 are set at the positions where the corresponding HRTEM micrographs, shown at the right side of Fig. 4, have been taken. At all the four positions, the lattice planes indexed as (101), $(10\bar{1})$ and (002) are clearly visible, resulting in a view along the (010) zone axis. Owing to the thickness of the sample, the quality of their appearance is decreasing from top to bottom, or 1 to 4, respectively. For further illustration of the similar crystalline orientation, fast fourier transforms (FFTs) have been calculated from images 1 to 4. Their center details are shown as insets in the HRTEM images. Apart from their similarity, two features deserve attention:

First, the FFT in image 2 shows spots adjacent to (002) and its related reflections. This is attributed to the slightly rotated area at the left side of the HRTEM image which is

Fig. 2 Comparison of TiO₂ tube length of three samples anodized at different voltages. Higher voltages lead to increasing length. Note the gold particles stemming from SEM characterization at the top of the 20 and 25 V samples

Fig. 3 BF (left) and DF (right) images show typical grains found in samples anodized at 15 V (a, b), 20 V (c, d), and 25 V (e, f). The arrow in image c shows that the sample has been cut at this position. Corresponding ED patterns are given as insets in the BF images and the reflections which have been taken for the according DF image, namely

partly hidden by the FFT inset. As it is visible in the BF image, this part is near the edge of the nanotube, which points toward some changes in crystal orientation in this

(200) (15 V), (101) (20 V) and (101) (25 V) of anatase, are marked. Crystals which are slightly rotated to each other, but whose reflections still lie within the aperture, appear bright in the DF image. Moiré patterns are visible here, too. Selected area diffraction aperture for ED patterns corresponds to a sample area of about $0.3 \mu\text{m}^2$ (Color figure online)

part of the tube wall. The second interesting feature is visible when comparing the FFT of image 4 to the other three FFTs. It is rotated by 2° , which means that the bottom

Fig. 4 Crystallinity of a tube wall. The left side shows a BF image of a nanotube from the 20 V sample which appears to be cut into halves lengthwise and has an orientation close to $\langle 010 \rangle$ zone axis. HRTEM micrographs 1–4 have been captured along the tube, and details of their FFTs in the middle show a similar orientation. In area 4, the crystal is rotated about 2° compared to the first three areas

of the tube is composed of a crystal slightly rotated compared with the rest of the tube. The remaining reflections which do not belong to the main lattice show the presence of smaller crystallites which can be part of the tube wall or may be located in front or behind the investigated tube.

To get further impressions about the crystallographic appearance of the tube walls, areas have been sought where these parts were visible edge-on. Figure 5a shows an area of the 25 V sample where the tube wall is clearly recognizable. The viewing direction is parallel to the $\langle \bar{1}\bar{1}1 \rangle$ crystallographic axis. A continuous visibility of the (011) lattice planes indicates further material with nearly similar orientation. The surface of the tube wall is faceted (emphasized by white lines) and terminated with (101) planes, indicating a tube morphology with minimized surface energies [25]. Wall thickness can be estimated to about 7–10 nm with some visible variation.

Another important feature concerning the connection between adjacent nanotubes is shown in Fig. 5b, which has been taken at the 15 V sample. To get a better impression of the surveyed area, its inset (Fig. 5c) shows the silhouette of the tube end as depicted in Fig. 5b. The black arrow points at a direct junction of two nanotubes which clearly show the same crystallographic orientation. (101) lattice planes of the tubes possess a direct contact. This area suggests that the present material either separated into two tubes or that two adjacent nanotubes grew together during annealing. As already indicated in the DF images of Fig. 3, annealing also caused the same crystal orientation in groups of adjacent nanotubes. A dashed white line in

Fig. 5b points out a small part of the tube wall which is slightly rotated by 4° against the remaining area. This means that some of the rotated crystals which have been observed by Moiré fringes may also be caused by minor bending effects within the tubes.

In order to evaluate the suitability of the nanotube arrays for applications in hybrid solar cells, they were sensitized with the widely used ruthenium dye Z907 and infiltrated with P3HT, a hole conducting, highly absorbing conjugated polymer, well known from applications in fully organic bulk heterojunction solar cells [26, 27]. Figure 6 shows I–V curves of a typical device, where the solid line represents the cell tested under simulated solar illumination. Only moderate power conversion efficiencies (PCEs) of $\sim 0.2\%$ are found, which is mainly caused by the small short circuit current densities (I_{SC}), whereas the cells show reasonable open circuit voltages (V_{OC}) between 0.5 and 0.55 V and high fill factors (FFs) of around 60 %.

Discussion

One of the most important questions of the foregoing analysis is the conductivity of the TiO_2 nanotubes based on a purposive view on material properties. This is of particular interest when using TiO_2 nanotubes as structured layer in dye-sensitized or hybrid polymer-metal oxide solar cells. In this regard, the elaborated results are very promising. All three anodization voltages resulted in grain sizes which exceed the findings of previous studies. Albu et al. [19] as

Fig. 5 **a** HRTEM micrograph of a tube wall of the 25 V sample shows faceting with a surface in $\langle 101 \rangle$ direction. This is known to be a preferred orientation due to minimized surface energies. **b** HRTEM micrograph of a tube end of the 15 V sample. The area marked by a dashed white line shows a small crystal rotated by about 4° against the rest of the tube. The black arrow points out the connection to an adjacent tube. *Inset c* clarifies the tube's boundaries

Fig. 6 Current density-voltage characteristic of a typical hybrid solar cell with P3HT as hole conductor based on TiO_2 nanotubes anodized at 25 V. The solid line corresponds to illumination with simulated solar light, whereas the dashed line is the I-V curve measured in the dark and shifted by the photocurrent measured under solar illumination

well as Li et al. [16] observed and expected large crystals of more than 100 nm, although the former conducted TEM measurements only on single nanotubes detached from the substrate and the latter assumed large crystals because of an absent peak broadening in XRD spectra. However, both investigations have been conducted at considerably larger structures (length 12–25 μm ; diameter ~ 150 nm) than the ones presented here. Hsiao et al. [15] also used larger structures during their research and derived grain sizes of 35 (± 1) nm from the Debye-Scherrer equation applied to their XRD patterns. They, as well as Albu et al., observed a random crystal orientation. From our observations by ED, DF imaging, and HRTEM, we could show that there is a strong correlation of the crystal orientation within one cluster of nanotubes. Further investigation is required to

provide proof of a possible tendency toward tube surfaces terminating with $\langle 101 \rangle$ planes.

As mentioned previously, large crystallites along the tube walls not only facilitate excellent electron conductivity from top to bottom of the tube, but the lateral expansion of same crystal orientations can also be beneficial to charge transport. This might be the case, e.g., if the charge transfer from one tube end to the electrode is blocked for any reason. Here, the electrons can easily circumvent the affected contact by conduction to an adjacent nanotube. In case of polycrystalline material, with grain sizes of 5–15 nm, charge trapping resulting in a conductivity-restraining potential or increased charge recombination would be inevitable. One remaining question is, how much of an impact on conductivity is made by bending as well as small crystal rotations along the tube walls. However, this should be only a minor decline compared to an alternative appearance of distinct grain boundaries.

Another point which was shown in our study is the sample structure's dependence on the anodization voltage. Increasing the voltage resulted in an increased tube length. Wider tube diameters and thicker tube walls as predicted in previous studies [17] could not be discerned with absolute certainty. What in turn could be observed is an increasing crystal size at increased anodization voltage. This results in a potential trade-off; for many applications, a high surface area of the TiO_2 nanotubes is desired. Taking into account decreasing tube dimensions like lower pore-to-pore distance and tube wall thickness at lower voltages, these would basically be the favored ones. However, as these applications often are in need of good conductivity, higher anodization voltages would be preferable. In the end, a suitable compromise ought to be found in an empirical

way, although the effect of other anodization parameters like bath temperature or electrolyte concentration should not be disregarded. It is obvious that, at least concerning the lower limit, extreme anodization voltages are not expedient.

Evaluating these results, it must be pointed out that TEM sample preparation is rather harsh, and mechanical handling or ion milling can induce damage or bending of the tube structure. This means that the reported crystalline appearance may be worse than it is in an untreated sample.

The low photocurrents of our P3HT-based hybrid solar cells can be attributed to two main issues. First, we did not optimize the structure filling, which most likely leads to the lower parts of the relatively long tubes being not infiltrated with P3HT. Thus, the resulting interfacial area between polymer and metal oxide is reduced. In addition, because of being sensitized with Z907, the TiO_2 that is not covered with P3HT is filtering light. Consequently, the light intensity is reduced at the sites where charges are actually separated, since incident light goes through the lower part of the nanotubes first. Second, more importantly, the interface between TiO_2 and P3HT is not optimized, probably resulting in a comparatively low exciton-to-charge conversion efficiency. Even though Z907 has proven highly efficient in solid-state dye-sensitized solar cells, other sensitizers appear to be better suited for applications with P3HT [23, 28]. For our preliminary experiments, however, we focused on the well-known standard material Z907 since its properties have been extensively described in the literature [29]. Besides, for the sake of simplicity, we did not subject the nanotubes to an additional TiCl_4 treatment or use any additives like 4-tert-butylpyridine or lithium salts, all of which are known to have positive effects on the cell's V_{OC} and especially I_{SC} [30, 31].

Nevertheless, we find FFs of around 60 % for our solar cells, which are remarkable within the aforementioned context. High FFs indicate slow charge carrier recombination and high and balanced charge carrier mobilities, which prevent the build-up of space charge regions [32, 33]. This is especially interesting when comparing these values to FFs reported for solar cells based on mesoporous TiO_2 and P3HT. Even though significantly higher V_{OC} and I_{SC} have been reported for such systems, the FF appears to be smaller there. Coakley et al. [34] reported a FF of 51 % for a solar cell with I_{SC} of 1.4 mA/cm^2 and V_{OC} of 0.72 V, i.e., much higher PCE than ours. Zhu et al. [35] could show PCEs of 2.6 % with mesoporous TiO_2 and P3HT, using organic dyes and additives. There, they found an even higher FF of 61 %. However, these high FFs were possible only for the ideal combination of additives, whereas FFs between 29 and 55 % have been reported if no or only one type of additive was used. Still lower FFs are present when directly blending TiO_2 nanoparticles with P3HT [36, 37].

Mor et al. [7] investigated TiO_2 nanotube arrays which are closely related to our system. While focusing on the influence of differently concentrated dyes, the measured FFs in that study are between 50 and 70 %.

We assume that in general anodized TiO_2 nanotubes feature larger crystals than those which occur in mesoporous TiO_2 . In addition, areas of similar oriented tubes are present depending on an existing contact between them. This results in high electron mobility. In contrast, average grain sizes in mesoporous TiO_2 are expected to be in the range of only 10–30 nm and do not exceed the diameter of individual nanoparticles [38]. Accordingly, considerably slower electron transport is expected in these structures.

Finally, the high diode quality of solar cells based on TiO_2 nanotube arrays is also apparent when comparing the I–V curve under illumination with the curve measured in the dark and shifted by I_{SC} , shown as dashed line in Fig. 6. For an ideal solar cell without recombination losses, these curves should overlay [39]. Even though this is not the case for our solar cells, the main difference lies in the higher virtual V_{OC} of the shifted dark curve, whereas the general shape of the curves is very similar. This indicates only small recombination losses.

Conclusion

Our TEM analysis on anodized TiO_2 nanotubes shows that they possess an anatase crystal structure and grain sizes considerably exceeding anticipated values, with possible extents of more than 300 nm along tube walls, which is remarkable at tube lengths of around 500 nm. Nearly similar oriented, though slightly rotated crystals have been found over wide areas. This has to our knowledge never been reported for nanostructured TiO_2 anatase system so far and can be explained by inter-tube connections which enable an extension of crystal grains across tube edges. These features provide good preconditions for the transfer of electrons toward the electrode, as was demonstrated by our solar cell measurements. In addition to crystal properties, the dependence between anodization voltage and tube dimensions, i.e., length and to a certain extent wall thickness, meaning longer tubes and thicker tube walls for higher voltages, was shown.

All the above findings lead to the conclusion that the efforts of implementing this tube system into sophisticated applications like hybrid solar cells should be well rewarding, since performance is expected to be excellent after further optimization of dye/polymer combination and respective treating. In the end, electrons have to be removed swiftly from interfaces to avoid charge recombination and realize efficient and loss-free photo-current generation.

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