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Thomas Cossuet, Laetitia Rapenne, Gilles Renou, Estelle Appert, Vincent Consonni. Template-Assisted Growth of Open-Ended TiO₂ Nanotubes with Hexagonal Shape Using Atomic Layer Deposition. *Crystal Growth & Design*, 2021, 21 (1), pp.125-132. 10.1021/acs.cgd.0c00952 . hal-03102060

HAL Id: hal-03102060

<https://hal.science/hal-03102060>

Submitted on 7 Jan 2021

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Template-Assisted Growth of Open-Ended TiO₂ Nanotubes with Hexagonal Shape Using Atomic Layer Deposition

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ABSTRACT

TiO₂ nanotubes have emerged as potential building blocks in nanostructured solar cells and photocatalytic devices, but the improvement of their crystalline quality and morphological control still requires further development. We report an original fabrication process to form open-ended TiO₂ nanotubes in the framework of the positive template-assisted growth using ZnO nanowires. The process involves the combination of atomic layer deposition with post-deposition thermal treatment in air at moderate temperature to crystallize an amorphous TiO_x layer into a soluble, cubic-Zn₂TiO₄ shell on the top face of ZnO nanowires and an insoluble, anatase-TiO₂ shell with large-sized domains on their sidewalls. The differential crystallization process originates from the differential reactivity on the polar *c*- and nonpolar *m*-plane surfaces of ZnO nanowires, further enhanced by the different thickness of the amorphous TiO_x layer. Following chemical etching, open-ended TiO₂ nanotubes exhibit hexagonal shape and high crystalline quality with sharp, well-oriented walls. These findings open the way for integrating high quality open-ended TiO₂ nanotubes with tunable length and wall thickness on a wide range of substrates. The present approach can further be developed to form other types of nanotubes and original nanowire heterostructures with highly localized, distinct phases for the shell using one simple thermal treatment.

KEYWORDS

Titanium Dioxide; Nanotubes; Template-assisted growth; Differential crystallization; Core-shell heterostructures; Transmission-electron microscopy.

1. INTRODUCTION

As a long-term stable, corrosion-resistant compound semiconductor with a wide band gap energy around 3 eV and suitable band edge positions, titanium dioxide (TiO_2) offers a large number of assets for photo-catalysis and energy conversion and storage.¹⁻² In most of these applications, the increase in the specific surface area by using nanostructures is of high interest for maximizing the light absorption and the efficiency of the chemical reactions with the medium. Among all the types of nanostructures, the form of nanotubes (NTs) exhibiting a high aspect ratio with a hollow inner channel has emerged as an invaluable structure in these applications.³⁻⁵ The synthesis of TiO_2 NTs can basically be achieved by the three following methods:⁶ i) electrochemical anodization of titanium foils/thin sheets,⁷⁻⁸ ii) hydro-/solvo-thermal growth in concentrated sodium hydroxide medium,⁹⁻¹⁰ and iii) template-assisted growth using sacrificial layers.¹¹⁻¹² The template-assisted growth has the great advantage to readily form TiO_2 NTs with a broad range of dimensions and with a high uniformity by simply tuning the morphology and size of the templates. It is further compatible with a large number of substrates including silicon and glass in contrast to the electrochemical anodization process. The most widely used positive template-assisted growth is based on the coating of TiO_2 on the outer surfaces of the templates and further selective wet chemical etching to form NTs. Hoyer *et al.* first reported the template-assisted growth of TiO_2 NTs by electrochemical deposition by using an ordered alumina template with a positive polymer mold that can be dissolved by acetone.¹¹ In addition to multi-walled carbon NTs, the use of ZnO nanowires (NWs) for the positive assisted-template growth of TiO_2 NTs has received an increasing interest in the last decade. The formation of ZnO NWs by the low-cost chemical bath deposition (CBD) technique operating at low-temperature and in aqueous solution represents an inexpensive method to fabricate highly reproducible positive templates.¹³

Basically, two general approaches have been established to form TiO_2 NTs from the ZnO NW templates. Lee *et al.* first reported the liquid phase deposition of TiO_2 NTs by immersing the ZnO NW template into an aqueous solution consisting of $(\text{NH}_4)_2\text{-TiF}_6$ and boric acid.¹⁴ As such, according to a simultaneous process, the precipitation of TiO_2 in the form of NTs was achieved while the dissolution of ZnO NWs operated. The present one-step approach has had a great success to form TiO_2 NTs, which

have mainly been integrated into photocatalytic devices¹⁵ and nanostructured solar cells.¹⁶⁻¹⁸ However, the resulting TiO₂ NTs following that one-step approach are polycrystalline and easily contaminated with residual precipitates. Later, Qiu *et al.* reported the deposition of TiO₂ shells by sol-gel process using spin/dip coating and layer-by-layer growth on ZnO NW templates and their selective wet chemical etching in hydrochloric acid led to the formation of TiO₂ NTs.¹⁹⁻²¹ The present double-step approach has had a great promise to form TiO₂ NTs, which have also been integrated into solar cells.²¹⁻²³ Nevertheless, the resulting TiO₂ NTs are also polycrystalline because sol-gel processes have mostly been used. Furthermore, an additional chemical step is required to form open-ended TiO₂ NTs, either through a final selective wet chemical etching or through an intermediate chemical capping on the top *c*-faces of ZnO NWs by using sodium citrate for example.²⁴ The structural quality of TiO₂ NTs using the double-step approach has thus been limited by the use of sol-gel process to form the TiO₂ shells over ZnO NW templates.

Atomic layer deposition (ALD) is a well-known technique to form highly conformal deposits over high aspect ratio surfaces like nanoporous materials owing to the self-saturating nature of the chemisorption and surface reactions.²⁵⁻²⁶ The fabrication of porous nanostructured metal oxides like interconnected nanoparticle chains using ALD and calcination was developed on multi-walled carbon NT templates.²⁷ On the one hand, the defective structure of multi-walled carbon NTs enhances the nucleation rate of the ALD processes, but, on the other hand, it results in the formation of defective TiO₂ interconnected nanoparticle chains with a self-supporting morphology.²⁸ In that sense, the use of ALD has a great promise, but the defective structure of multi-walled carbon NTs is not optimal. Recently, the fabrication of epitaxial ZnO / TiO₂ core-shell NW heterostructures using ALD and post-deposition thermal treatment for nanostructured solar cells have opened the way for developing more innovative heterostructures within such an approach.²⁹ The double-step process is based on the initial ALD of the amorphous TiO_x layer on ZnO NWs and its subsequent crystallization into an epitaxial anatase-TiO₂ shell using post-deposition thermal treatment. That process is expected to strongly depend on the conditions used by ALD and post-deposition thermal treatment, but this has not been explored yet.

In this work, we present a double-step approach to fabricate open-ended TiO₂ NTs in the framework of the positive template-assisted growth using ZnO NW arrays grown by CBD. The process involves

the combination of ALD to form an amorphous TiO_x shell over ZnO NW arrays and a post-deposition thermal treatment in air at moderate temperature. The crystallization process of the amorphous TiO_x shell on the *m*-plane sidewalls of ZnO NWs is found to differ from the one on their top *c*-face during the post-deposition thermal treatment. This particularity is used to form open-ended TiO_2 NTs with a hexagonal shape and a high crystalline quality following a selective wet chemical etching without any additional chemical step in the fabrication process.

2. EXPERIMENTS

2.1. Synthesis of TiO_2 nanotubes. Polycrystalline ZnO seed layers were deposited by dip coating on silicon using a sol-gel process. Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Sigma-Aldrich) and monoethanolamine (MEA, Sigma-Aldrich) were dissolved in pure ethanol to prepare the 375 mM equimolar solution of chemical precursors. The samples were slowly dipped into the equimolar solution and gently pulled out under controlled atmosphere at a withdrawal speed of 3.3 mm/s. They were subsequently annealed successively on two hot plates kept at 300 °C for 10 min and at 500 °C for 1 hour, respectively. ZnO NW arrays were grown on the polycrystalline ZnO seed layers by CBD. Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich) and hexamethylenetetramine (HMTA, Sigma-Aldrich) were dissolved in deionized water to prepare the 30 mM equimolar solution of chemical precursors. The samples were placed face down in a sealed reactor located in a regular oven kept at 90 °C for 3 hours. The ZnO NW templates were then covered with an amorphous TiO_x layer by ALD using a Cambridge Nanotech F200 Fiji reactor maintained at 200 °C and at 11 mTorr. Tetrakis dimethylamino titanium beforehand heated at 75 °C and H_2O were sequentially injected for 0.1 s in the chamber to alternately introduce the titanium and oxygen chemical precursors, respectively. A purge of 10 s was used after each pulse. The samples were eventually annealed in air in an oven kept at 350 °C for 3 hours for the crystallization of the amorphous TiO_x layer. The selective wet chemical etching process was achieved by dipping the samples for 30 s into a beaker containing an aqueous solution kept at room temperature and at a low pH of 1.7 using hydrochloric acid. The samples were eventually rinsed with deionized water and dried under a nitrogen flow.

2.2. Characterization Techniques. Field-emission gun scanning electron microscopy (FESEM) imaging was performed with a ZEISS Ultra 55 FESEM instrument. The surface of ZnO core-shell NW heterostructures was scratched with a diamond tip and the residues were put on a carbon film placed over a copper grid to prepare the specimens for transmission electron microscopy (TEM). TEM and high-resolution TEM (HRTEM) imaging was achieved with a JEOL 2010 LaB₆ microscope operating at 200 kV with a 0.19 nm point-to-point resolution. Energy-dispersive x-ray spectroscopy (EDS) measurements were collected by TEM with the present microscope. Automated crystal phase and orientation mapping was performed in a JEOL 2100F FEG microscope equipped with a precession module through the automated indexing of electron diffraction patterns for which a precession angle of 1.16 ° was used. The electron diffraction patterns were recorded by using a rate of 100 frames per second with a step size of 1 nm, resulting in a total acquisition time of 25 min per map.

3. RESULTS AND DISCUSSION

A schematic of the fabrication process of open-ended TiO₂ NTs involving five successive steps is presented in **Figure 1**.

Figure 1. Schematic diagram representing the five steps required for the fabrication process of open-ended TiO₂ NTs from a positive template made of ordered ZnO NW arrays.

A 40 nm-thick polycrystalline ZnO seed layer is first deposited by sol-gel process using dip coating, as seen in **Figure 2a,b**.³⁰ It consists of an ensemble of compact grains with non-polar, semi-polar, and polar orientations.³¹ In the second step, vertically aligned ZnO NWs with a typical mean diameter and length of 80 and 950 nm, respectively, are grown by CBD to create the positive template, as seen in **Figure 2c,d**.³² They preferentially nucleate on the grains with semi-polar and polar orientations in the textured seed layer.³¹ Their length can readily be tuned over a broad range of 100 nm – 10 μ m by adjusting the concentration of chemical precursors³²⁻³³ or by using chemical additives like polyethyleneimine³⁴⁻³⁵ to reduce their radial growth. In the third step, the growth of the amorphous TiO_x layer is achieved at 200 °C by ALD on the positive template of ZnO NWs. It typically results in the deposition of a conformal shell on the *m*-plane sidewalls of ZnO NWs from their top to their base. However, it should be noted here that the conformality by ALD is not perfect. As a result, the amorphous TiO_x layer is slightly thicker (*i.e.* a couple of nanometers more) on the top *c*-face of ZnO NWs than on their *m*-plane sidewalls, which is a key parameter in the present fabrication process. The ALD processes are driven by the self-saturating nature of the chemisorption and surface reactions to ensure a perfect conformality.²⁶ Nevertheless, given that the polar *c*-plane is much more reactive than the non-polar *m*-planes in ZnO,³⁶ it is believed that the sticking probability during the ALD process of the amorphous TiO_x layer is larger on the top *c*-face of ZnO NWs, resulting in a slightly larger thickness. In particular, the configuration of O-H groups on the surface strongly depends on the nature of the involved crystallographic plane.³⁶ The thickness of the TiO_x shell grown by ALD can be varied from a couple of nanometers to several tens of nanometers by simply adjusting the number of cycles used during the ALD process.³⁷⁻³⁸ In the fourth step, the ZnO core-shell NW heterostructures are annealed at 350 °C for 3 hours during a post-deposition thermal treatment in air, as seen in **Figure 2e,f**.

Figure 2. (a, c, e) Top-view and (b, d, f) cross-sectional view FESEM images of (a, b) polycrystalline ZnO seed layer grown by dip coating using a sol-gel process (*i.e.* first step), (c, d) ZnO NWs grown by CBD (*i.e.* second step), and (e, f) ZnO core-shell NW heterostructures grown by ALD (*i.e.* third step) and annealed at 350 °C for 3 hours in air (*i.e.* fourth step).

In order to investigate in detail the structural properties of ZnO core-shell NW heterostructures, TEM-based experiments were performed over a large number of nano-objects, and the overall analysis is presented in **Figures 3** and **4** on a typical object. The conformality of the shell deposited by ALD on the *m*-plane sidewalls of ZnO NWs is very high following the post-deposition thermal treatment, as seen by the TEM image in **Figure 3a**. An overall thickness value of about 10 nm is typically measured. In contrast, the shell on the top *c*-face of ZnO NWs is thicker by a couple of nanometers more and reach a typical value of about 15 nm. In that sense, the different thickness of the shell following the ALD process is kept after the post-deposition thermal treatment. Given that the TEM imaging is spatially localized on the nanometer scale, ASTAR measurements were carried out to investigate the structural properties of ZnO core-shell NW heterostructures on a larger scale. To decrease dynamical effects and enhance the indexing quality of electron diffraction patterns, the 2 nm-sized incident electron beam was precessed around the optical axis. The scanning of the precessed electron beam synchronized with the recording of the experimental electron diffraction patterns at each location was achieved with a step of 1 nm over the area of interest. Following an automated procedure aiming at carefully comparing and matching the experimental and theoretical electron diffraction patterns as simulated for every expected crystalline phases and for a large number of orientations,³⁹⁻⁴⁰ the identification of both crystalline phases and orientations in the ZnO core-shell NW heterostructures was inferred with a high degree of precision. The corresponding map of the crystalline phases of ZnO core-shell NW heterostructures is presented in **Figure 3b**. Very interestingly, the amorphous TiO_x shell grown by ALD crystallizes into two different structures that are highly localized and spatially separated following the post-deposition thermal treatment. On the *m*-plane sidewalls of ZnO NWs, the shell exhibits a single anatase-TiO₂ phase belonging to the *I4₁/amd* space group, as shown by the electron diffraction pattern in **Figure 3d** collected on the position *B* in **Figure 3b**. Only the anatase-TiO₂ phase is detected from the top to the base of ZnO

NWs and its thickness is constant with a value of around 10 nm. No sign for the presence of rutile-TiO₂ phase has been revealed. Additionally, the present shell exhibits some domains with sizes that are much larger than its thickness and with a limited number of orientations, as revealed in **Figure 4**. Given that the ALD technique generally leads to the deposition of poorly oriented spherical grains with a size that is typically of the same order of magnitude as its thickness, the oriented large-size domains indicate local orientation relationships with the sidewalls of ZnO NWs through a process of local epitaxy. The presence of these large-sized domains with a high crystalline quality offers a strong asset as the coming constituting blocks in the walls of TiO₂ NTs. The present ZnO / TiO₂ core-shell NW heterostructures have largely been used as electron transporting materials in nanostructured solar cells.^{37-38, 41-42} In contrast, a single spinel cubic-Zn₂TiO₄ phase belonging to the *Fd3m* space group is specifically identified on the top *c*-face of ZnO NWs, as shown by the electron diffraction pattern in **Figure 3e** collected on the position *C* in **Figure 3b**. The detection of that phase in the present case is technically challenging by standard characterization techniques because its overall amount is very small. The formation of that spinel phase was shown from ZnO / Ti core-shell NW heterostructures⁴³ and from ZnO / TiO₂ core-shell NW heterostructures⁴⁴ when an additional thermal treatment at a much higher temperature ranging from 800 to 900 °C activate the solid-state reaction to form multi-twinned Zn₂TiO₄ NWs. It is expected here that the annealing temperature of 350 °C is sufficient to activate the interfacial solid-solid reaction between the ZnO NW and TiO_x amorphous shell only on their top *c*-face to form the spinel cubic-Zn₂TiO₄ phase. The present polar *c*-planes are composed of the stack of successive zinc cation and oxygen anion layers.³⁶ They have a high surface energy⁴⁵ and are known to be highly reactive, which could favour the intermixing between the different chemical elements. In contrast, the nonpolar *m*-planes are composed of the stack of successive layers with an equal number of zinc cations and oxygen anions.³⁶ They have a much lower surface energy⁴⁶ and are generally more stable. The present data further show that the nature of the crystallization process strongly depends on the thickness of the amorphous TiO_x shell and on its location, either on the polar *c*- or non-polar *m*-planes of ZnO to favour a differential reactivity. As the thickness is considerably decreased at nanoscale dimensions, the crystallization process further requires more and more energy and hence higher effective annealing temperatures to operate. In the present fourth step, a couple of nanometers of difference in the thickness

of the amorphous TiO_x shell grown by ALD in that range can readily switch the crystallization process from an anatase- TiO_2 phase to a cubic- Zn_2TiO_4 phase on the top c -face of ZnO NWs for the same annealing temperature. The resulting ZnO NW heterostructures with two different TiO_2 and Zn_2TiO_4 shells are of high potential for photocatalytic devices⁴⁷ and may enhance the degradation rate in the present double shell configuration. In contrast, when the thickness of the amorphous TiO_x layer is smaller, only the anatase- TiO_2 phase is formed on the top as recently reported in Ref. ²⁹. The resulting ZnO / TiO_2 core-shell NW heterostructures are of high interest for nanostructured solar cells for instance.⁴⁸ In the present conditions of post-deposition thermal treatment for 3 hours at 350 °C in air, the thickness-dependent phase transition is abrupt and proceeds around 12 - 15 nm.

Figure 3. (a) Typical TEM image of a ZnO core-shell NW heterostructure. (b) Corresponding crystalline phase map of the ZnO core-shell NW heterostructure using ASTAR measurements. The wurtzite-ZnO, anatase- TiO_2 and cubic- Zn_2TiO_4 phases are shown in red, blue and green, respectively. (c, d, e) Corresponding experimental electron diffraction patterns recorded at the positions A, B and C, respectively. The red, blue and green circles indicate the theoretical electron diffraction patterns of the wurtzite-ZnO, anatase- TiO_2 and cubic- Zn_2TiO_4 phases.

Figure 4. Crystalline orientation maps of the wurtzite ZnO, anatase TiO₂ and cubic Zn₂TiO₄ phases within the ZnO core-shell NW heterostructure along the X, Y and Z axes using ASTAR measurements. The color scales for wurtzite ZnO, anatase TiO₂ and cubic Zn₂TiO₄ are presented in the insets.

Very importantly, the anatase-TiO₂ and cubic-Zn₂TiO₄ phases do not exhibit the same stability in acidic medium, which is another key parameter in the present fabrication process. In the fifth step, the ZnO NW heterostructures with the TiO₂ and Zn₂TiO₄ shells are immersed for 30 s into an aqueous solution kept at room temperature and at a low pH of 1.7 using hydrochloric acid for a selective wet chemical etching. Owing to the chemical instability of the cubic-Zn₂TiO₄ phase in acidic medium, the Zn₂TiO₄ shell on the top *c*-face of ZnO NWs is dissolved in hydrochloric acid along with the entire ZnO NW. In contrast, the anatase-TiO₂ shell on the *m*-plane sidewalls of ZnO NWs is not affected in hydrochloric acid, forming in turn the open-ended TiO₂ NTs with the walls being composed of the large-sized domains with a high crystalline quality. Typical TEM and FESEM images of open-ended TiO₂ NTs are presented in **Figures 5** and **6** along with TEM and HRTEM images of a representative nano-object in **Figure 7**.

Figure 5. Typical top-view TEM image of open-ended TiO₂ NTs dispersed on a carbon film on copper TEM grid.

Figure 6. Typical top-view FESEM images of (a) open-ended TiO₂ NT with a hexagonal shape, (b) open-ended TiO₂ NTs with a hexagonal and elongated shape, (c) open-ended TiO₂ NT with a different shape resulting from ZnO NW initial coalescence, and (d) open-ended TiO₂ NT with a hexagonal shape surrounded by un-completely open TiO₂ NTs. The scale bar corresponds to 100 nm.

The open-ended TiO₂ NTs have an overall hexagonal shape and a high crystalline quality coming from the use of the ALD process. The TEM image of TiO₂ NTs dispersed on the grid shows that they are all open on their top, as seen in **Figure 5**. No parasitic ZnO phase is detected using selected area electron diffraction, indicating a complete dissolution of ZnO NWs owing to their high solubility at the low pH of 1.7.³² Instead, a K_α line with a small intensity is attributed to residual Zn in the TEM-EDS spectra, as shown in Figure S1 of Supporting Information. Further rinsing steps can readily be used to remove the Zn contamination. Correlatively, the FESEM image of TiO₂ NTs on silicon also reveals that most of the TiO₂ NTs are open on their top with the occurrence of much brighter walls, as seen in **Figure 6**. Some of them with a hexagonal shape have a very dark inner channel, when the TiO₂ NT is vertically aligned on the substrate and when the ZnO seed layer has been dissolved in hydrochloric acid, as seen in **Figure 6a**. Others present a less dark inner channel, when the TiO₂ NT is tilted with respect to the normal to the substrate and thus when its base on silicon is not visible. Others exhibit an elongated hexagonal shape, as seen in **Figure 6b**. Overall, the homogeneity of TiO₂ NT arrays is drastically dependent upon the distribution of ZnO NW arrays acting as the positive template. For instance, the presence of coalesced ZnO NWs result in the formation of open-ended TiO₂ NTs with a different shape, as seen in **Figure 6c**. Eventually, others may not have completely been open during the selective wet chemical etching, specifically the ones with a shorter length as indicated in the proximity of the open-ended TiO₂

NT with a hexagonal shape in **Figure 6d**. This inhomogeneity may come from the differential crystallization process over ZnO NWs with a much shorter length where the amorphous TiO_x layer could be thinner. More importantly, the walls of open-ended TiO_2 NTs are sharp, because the anatase- TiO_2 shell on the sidewalls of ZnO NWs is composed of domains with large sizes. They are also oriented along given directions, because the domains composing the anatase- TiO_2 shell exhibit a limited number of orientation relationships with the sidewalls of ZnO NWs through a local epitaxy process. For instance, some walls are composed of (101) anatase- TiO_2 planes, as seen in **Figure 7**. This is in strong contrast to the alternative processes using wet chemistry, growing a polycrystalline TiO_2 shell over the ZnO NWs that are made of randomly oriented domains with a much smaller size.^{14, 19} Furthermore, the wall thickness of the open-ended NTs lies in the range of 9 – 10 nm and is thus correlated directly with the thicknesses of the amorphous TiO_x shell grown by ALD and of the TiO_2 shell following the post-deposition thermal treatment. This offers a great opportunity as well to control the wall thickness with a high degree of precision and to reduce it as much as possible. The length of the open-ended TiO_2 NTs around 950 nm is further correlated with the length of ZnO NWs grown by CBD. Eventually, it is worth noticing that the fabrication process is compatible with the formation of open-ended TiO_2 NTs over a large number of substrates (*e.g.*, silicon, glass, ITO/glass, metal foils, sapphire) and does not use any chemical additives that may introduce chemical pollutants or alter the surface quality. The present process has further been illustrated in the case of the spontaneous growth approach to form ZnO NW arrays,³² but the selective area growth approach may also be employed to form ordered ZnO NW arrays and hence to gain a larger uniformity.⁴⁹⁻⁵⁰ The possibility to form open-ended TiO_2 NTs with an overall hexagonal shape, a higher crystalline quality, and well-oriented walls with a tunable small thickness is of high interest in photovoltaics and photocatalysis. Furthermore, the critical fourth step in the present process devoted to one simple thermal treatment is shown to result in the fabrication of NW heterostructures with highly localized, distinct phases for the shell, opening some perspectives in the field to design original NW heterostructures.

Figure 7 Top-view TEM image of an open-ended TiO_2 NT (left). Corresponding HRTEM image (center) with a Fourier-filtered enhancement (right) showing that the wall is composed of (101) anatase- TiO_2 planes.

4. CONCLUSIONS

In summary, we have developed an original fabrication process to form open-ended TiO_2 NTs in the framework of the positive template-assisted growth using ZnO NWs. The fabrication process benefits from the use of ALD coupled with a post-deposition thermal treatment in air at moderate temperature. It results in the formation of a soluble, spinel cubic- Zn_2TiO_4 shell located on the top c -face of ZnO NWs and an insoluble, conformal anatase- TiO_2 shell composed of domains with a large size that are highly oriented on the m -plane sidewalls of ZnO NWs. The differential crystallization process of the amorphous TiO_x shell originates from the differential reactivity on the polar c - and nonpolar m -plane surfaces of ZnO NWs that is further enhanced by its different thickness. Following an immersion into hydrochloric acid, the resulting open-ended TiO_2 NTs exhibit hexagonal shape and high crystalline quality with sharp and well-oriented walls without any additional chemical step in the fabrication process. These findings open the way for integrating high quality open-ended TiO_2 NTs with tunable length and wall thickness into nanostructured solar cells and photocatalytic devices with improved performances. The present approach is compatible with a wide range of substrates and can be extended to other types of NTs. It further highlights the possibility to design original NW heterostructures with highly localized, distinct phases for the shell using one simple thermal treatment.

ACKNOWLEDGEMENTS

This work was partly supported by the French Research National Agency through the project DOSETTE (ANR-17-CE24-0004) and by the Cross-Disciplinary Program of IDEX Université Grenoble Alpes (ANR-15-IDEX-02) through the project ECO-SESA. It has further benefited from the facilities, and the scientific and technical assistance of the CMTC characterization platform of Grenoble INP supported by the Centre of Excellence of Multifunctional Architected Materials (LabEx CEMAM) under the contract ANR-10-LABX-44-01 funded by the "Investments for the Future" Program.

ASSOCIATED CONTENT

Typical TEM-EDS spectrum recorded on open-ended TiO₂ NTs following the fifth step corresponding to the selective wet chemical etching (**Figure S1**).

REFERENCES

1. Fujishima, A.; Zhang, X. T.; Tryk, D. A. TiO₂ Photocatalysis and Related Surface Phenomena. *Surf. Sci. Rep.* **2008**, *63*, 515-582.
2. Zhang, Q. F.; Uchaker, E.; Candelaria, S. L.; Cao, G. Z. Nanomaterials for Energy Conversion and Storage. *Chem. Soc. Rev.* **2013**, *42*, 3127-3171.
3. Pang, Y. L.; Lim, S.; Ong, H. C.; Chong, W. T. A Critical Review on the Recent Progress of Synthesizing Techniques and Fabrication of TiO₂-Based Nanotubes Photocatalysts. *Appl. Catal. A-Gen.* **2014**, *481*, 127-142.
4. Nasr, M.; Eid, C.; Habchi, R.; Miele, P.; Bechelany, M. Recent Progress on Titanium Dioxide Nanomaterials for Photocatalytic Applications. *ChemSusChem* **2018**, *11*, 3023-3047.
5. Mor, G. K.; Varghese, O. K.; Paulose, M.; Shankar, K.; Grimes, C. A. A Review on Highly Ordered, Vertically Oriented TiO₂ Nanotube Arrays: Fabrication, Material Properties, and Solar Energy Applications. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2011-2075.
6. Roy, P.; Berger, S.; Schmuki, P. TiO₂ Nanotubes: Synthesis and Applications. *Angew. Chem.-Int. Edit.* **2011**, *50*, 2904-2939.
7. Zwilling, V.; Darque-Ceretti, E.; Boutry-Forveille, A.; David, D.; Perrin, M. Y.; Aucouturier, M. Structure and Physicochemistry of Anodic Oxide Films on Titanium and Ta6v Alloy. *Surf. Interface Anal.* **1999**, *27*, 629-637.
8. Zwilling, V.; Aucouturier, M.; Darque-Ceretti, E. Anodic Oxidation of Titanium and Ta6v Alloy in Chromic Media. An Electrochemical Approach. *Electrochim. Acta* **1999**, *45*, 921-929.
9. Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K. Formation of Titanium Oxide Nanotube. *Langmuir* **1998**, *14*, 3160-3163.
10. Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K. Titania Nanotubes Prepared by Chemical Processing. *Adv. Mater.* **1999**, *11*, 1307-1311.
11. Hoyer, P. Formation of a Titanium Dioxide Nanotube Array. *Langmuir* **1996**, *12*, 1411-1413.
12. Sander, M. S.; Cote, M. J.; Gu, W.; Kile, B. M.; Tripp, C. P. Template-Assisted Fabrication of Dense, Aligned Arrays of Titania Nanotubes with Well-Controlled Dimensions on Substrates. *Adv. Mater.* **2004**, *16*, 2052-2057.
13. Vaysieres, L. Growth of Arrayed Nanorods and Nanowires of ZnO from Aqueous Solutions. *Adv. Mater.* **2003**, *15*, 464-466.

14. Lee, J. H.; Leu, I. C.; Hsu, M. C.; Chung, Y. W.; Hon, M. H. Fabrication of Aligned TiO₂ Nanostructured Arrays Using a One-Step Templating Solution Approach. *J. Phys. Chem. B* **2005**, *109*, 13056-13059.
15. Yuan, J. J.; Li, H. D.; Gao, S. Y.; Lin, Y. H.; Li, H. Y. A Facile Route to N-Type TiO₂-Nanotube/P-Type Boron-Doped-Diamond Heterojunction for Highly Efficient Photocatalysts. *Chem. Commun.* **2010**, *46*, 3119-3121.
16. Charoensirithavorn, P.; Ogomi, Y.; Sagawa, T.; Hayase, S.; Yoshikawa, S. A. Facile Route to TiO₂ Nanotube Arrays for Dye-Sensitized Solar Cells. *J. Cryst. Growth* **2009**, *311*, 757-759.
17. Xu, C. K.; Shin, P. H.; Cao, L. L.; Wu, J. M.; Gao, D. Ordered TiO₂ Nanotube Arrays on Transparent Conductive Oxide for Dye-Sensitized Solar Cells. *Chem. Mater.* **2010**, *22*, 143-148.
18. Zhang, J.; Pauporte, T. One-Dimensional Self-Standing TiO₂ Nanotube Array Layers Designed for Perovskite Solar Cell Applications. *ChemPhysChem* **2015**, *16*, 2836-2841.
19. Qiu, J. J.; Yu, W. D.; Gao, X. D.; Li, X. M. Sol-Gel Assisted ZnO Nanorod Array Template to Synthesize TiO₂ Nanotube Arrays. *Nanotechnology* **2006**, *17*, 4695-4698.
20. Qiu, J. J.; Jin, Z. G.; Liu, Z. F.; Liu, X. X.; Liu, G. Q.; Wu, W. B.; Zhang, X.; Gao, X. D. Fabrication of TiO₂ Nanotube Film by Well-Aligned ZnO Nanorod Array Film and Sol-Gel Process. *Thin Solid Films* **2007**, *515*, 2897-2902.
21. Qiu, J. J.; Zhuge, F. W.; Lou, K.; Li, X. M.; Gao, X. D.; Gan, X. Y.; Yu, W. D.; Kim, H. K.; Hwang, Y. H. A Facile Route to Aligned TiO₂ Nanotube Arrays on Transparent Conducting Oxide Substrates for Dye-Sensitized Solar Cells. *J. Mater. Chem.* **2011**, *21*, 5062-5068.
22. Na, S. I.; Kim, S. S.; Hong, W. K.; Park, J. W.; Jo, J.; Nah, Y. C.; Lee, T.; Kim, D. Y. Fabrication of TiO₂ Nanotubes by Using Electrodeposited ZnO Nanorod Template and Their Application to Hybrid Solar Cells. *Electrochim. Acta* **2008**, *53*, 2560-2566.
23. Liu, Z. F.; Liu, C. C.; Ya, J.; Lei, E. Controlled Synthesis of ZnO and TiO₂ Nanotubes by Chemical Method and Their Application in Dye-Sensitized Solar Cells. *Renew. Energy* **2011**, *36*, 1177-1181.
24. Song, H.; Jo, K.; Jung, B. Y.; Jung, G. Y. Fabrication of Periodically Aligned Vertical Single-Crystalline Anatase TiO₂ Nanotubes with Perfect Hexagonal Open-Ends Using Chemical Capping Materials. *Nano Res.* **2014**, *7*, 104-109.
25. Detavernier, C.; Dendooven, J.; Sree, S. P.; Ludwig, K. F.; Martens, J. A. Tailoring Nanoporous Materials by Atomic Layer Deposition. *Chem. Soc. Rev.* **2011**, *40*, 5242-5253.
26. Cremers, V.; Puurunen, R. L.; Dendooven, J. Conformality in Atomic Layer Deposition: Current Status Overview of Analysis and Modelling. *Appl. Phys. Rev.* **2019**, *6*, 43.
27. Deng, S. R.; Kurttepel, M.; Cott, D. J.; Bals, S.; Detavernier, C. Porous Nanostructured Metal Oxides Synthesized through Atomic Layer Deposition on a Carbonaceous Template Followed by Calcination. *J. Mater. Chem. A* **2015**, *3*, 2642-2649.
28. Deng, S. R.; Verbruggen, S. W.; He, Z. B.; Cott, D. J.; Vereecken, P. M.; Martens, J. A.; Bals, S.; Lenaerts, S.; Detavernier, C. Atomic Layer Deposition-Based Synthesis of Photoactive TiO₂ Nanoparticle Chains by Using Carbon Nanotubes as Sacrificial Templates. *RSC Adv.* **2014**, *4*, 11648-11653.
29. Cossuet, T.; Appert, E.; Chaix-Pluchery, O.; Roussel, H.; Rapenne, L.; Renou, G.; Sauvage, F.; Consonni, V. Epitaxial TiO₂ Shell Grown by Atomic Layer Deposition on ZnO Nanowires Using a Double-Step Process and Its Beneficial Passivation Effect. *J. Phys. Chem. C* **2020**, *124*, 13447-13455.
30. Guillemin, S.; Appert, E.; Roussel, H.; Doisneau, B.; Parize, R.; Boudou, T.; Bremond, G.; Consonni, V. Controlling the Structural Properties of Single Step, Dip Coated ZnO Seed Layers for Growing Perfectly Aligned Nanowire Arrays. *J. Phys. Chem. C* **2015**, *119*, 21694-21703.
31. Cossuet, T.; Roussel, H.; Chauveau, J. M.; Chaix-Pluchery, O.; Thomassin, J. L.; Appert, E.; Consonni, V. Well-Ordered ZnO Nanowires with Controllable Inclination on Semipolar ZnO Surfaces by Chemical Bath Deposition. *Nanotechnology* **2018**, *29*, 11.
32. Parize, R.; Garnier, J.; Chaix-Pluchery, O.; Verrier, C.; Appert, E.; Consonni, V. Effects of Hexamethylenetetramine on the Nucleation and Radial Growth of ZnO Nanowires by Chemical Bath Deposition. *J. Phys. Chem. C* **2016**, *120*, 5242-5250.
33. Sugunan, A.; Warad, H. C.; Boman, M.; Dutta, J. Zinc Oxide Nanowires in Chemical Bath on Seeded Substrates: Role of Hexamine. *J. Sol-Gel Sci. Technol.* **2006**, *39*, 49-56.

34. Parize, R.; Garnier, J. D.; Appert, E.; Chaix-Pluchery, O.; Consonni, V. Effects of Polyethylenimine and Its Molecular Weight on the Chemical Bath Deposition of ZnO Nanowires. *ACS Omega* **2018**, *3*, 12457-12464.
35. Xu, C. K.; Shin, P.; Cao, L. L.; Gao, D. Preferential Growth of Long ZnO Nanowire Array and Its Application in Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2010**, *114*, 125-129.
36. Zuniga-Perez, J.; Consonni, V.; Lymperakis, L.; Kong, X.; Trampert, A.; Fernandez-Garrido, S.; Brandt, O.; Renevier, H.; Keller, S.; Hestroffer, K. et al. Polarity in GaN and ZnO: Theory, Measurement, Growth, and Devices. *Appl. Phys. Rev.* **2016**, *3*, 041303.
37. Law, M.; Greene, L. E.; Radenovic, A.; Kuykendall, T.; Liphardt, J.; Yang, P. D. ZnO-Al₂O₃ and ZnO-TiO₂ Core-Shell Nanowire Dye-Sensitized Solar Cells. *J. Phys. Chem. B* **2006**, *110*, 22652-22663.
38. Greene, L. E.; Law, M.; Yuhas, B. D.; Yang, P. D. ZnO-TiO₂ Core-Shell Nanorod/P3HT Solar Cells. *J. Phys. Chem. C* **2007**, *111*, 18451-18456.
39. Rauch, E. F.; Veron, M. Automated Crystal Orientation and Phase Mapping in Tem. *Mater. Charact.* **2014**, *98*, 1-9.
40. Midgley, P. A.; Eggeman, A. S., Precession Electron Diffraction - a Topical Review. *IUCrJ* **2015**, *2*, 126-136.
41. Xu, C. K.; Wu, J. M.; Desai, U. V.; Gao, D. Multilayer Assembly of Nanowire Arrays for Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2011**, *133*, 8122-8125.
42. Parize, R.; Katerski, A.; Gromyko, I.; Rapenne, L.; Roussel, H.; Karber, E.; Appert, E.; Krunks, M.; Consonni, V. ZnO/TiO₂/Sb₂S₃ Core-Shell Nanowire Heterostructure for Extremely Thin Absorber Solar Cells. *J. Phys. Chem. C* **2017**, *121*, 9672-9680.
43. Yang, Y.; Sun, X. W.; Tay, B. K.; Wang, J. X.; Dong, Z. L.; Fan, H. M. Twinned Zn₂TiO₄ Spinel Nanowires Using ZnO Nanowires as a Template. *Adv. Mater.* **2007**, *19*, 1839-1844.
44. Yang, Y.; Scholz, R.; Fan, H. J.; Hesse, D.; Gosele, U.; Zacharias, M. Multitwinned Spinel Nanowires by Assembly of Nanobricks Via Oriented Attachment: A Case Study of Zn₂TiO₄. *ACS Nano* **2009**, *3*, 555-562.
45. Wander, A.; Schedin, F.; Steadman, P.; Norris, A.; McGrath, R.; Turner, T. S.; Thornton, G.; Harrison, N. M. Stability of Polar Oxide Surfaces. *Phys. Rev. Lett.* **2001**, *86*, 3811-3814.
46. Wander, A.; Harrison, N. M. An Ab Initio Study of ZnO(10-10). *Surf. Sci.* **2000**, *457*, L342-L346.
47. Wan, L. Y.; Li, X. Y.; Qu, Z. P.; Shi, Y.; Li, H.; Zhao, Q. D.; Chen, G. H. Facile Synthesis of ZnO/Zn₂TiO₄ Core/Shell Nanowires for Photocatalytic Oxidation of Acetone. *J. Hazard. Mater.* **2010**, *184*, 864-868.
48. Consonni, V.; Briscoe, J.; Karber, E.; Li, X.; Cossuet, T. ZnO Nanowires for Solar Cells: A Comprehensive Review. *Nanotechnology* **2019**, *30*, 362001.
49. Wei, Y. G.; Wu, W. Z.; Guo, R.; Yuan, D. J.; Das, S. M.; Wang, Z. L. Wafer-Scale High-Throughput Ordered Growth of Vertically Aligned ZnO Nanowire Arrays. *Nano Lett.* **2010**, *10*, 3414-3419.
50. Consonni, V.; Sarigiannidou, E.; Appert, E.; Bocheux, A.; Guillemin, S.; Donatini, F.; Robin, I. C.; Kioseoglou, J.; Robaut, F. Selective Area Growth of Well-Ordered ZnO Nanowire Arrays with Controllable Polarity. *ACS Nano* **2014**, *8*, 4761-4770.

Template-Assisted Growth of Open-Ended TiO₂ Nanotubes with Hexagonal Shape Using Atomic Layer Deposition

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We report an original fabrication process of open-ended TiO₂ nanotubes that is based on the differential crystallization of the amorphous TiO_x layer grown by atomic layer deposition into a soluble Zn₂TiO₄ shell on the top face of ZnO nanowires and an insoluble epitaxial TiO₂ shell on their sidewalls following a simple thermal treatment.