

Rapid room temperature crystallization of TiO₂ nanotubes

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Abstract: The paper reports a very efficient and reproducible technique for room temperature crystallization of titanium dioxide in a record time of 5 minutes, by application of alternating voltage square pulses. The well aligned tubular formation of crystalline nanotubes is confirmed through various characterizations and the mechanism of crystallization is explained based on the pulse induced electrophilic-nucleophilic reaction. This ultrafast pulsed crystallization method provides a viable alternative for the widely used post fabrication thermal annealing and is highly applicable in device fabrication.

The ability to tune the optical and electrochemical properties of nanostructures is important for a variety of optoelectronic devices, sensing and photo catalytic applications^{1,2,3}. TiO₂ nanotube (TONT), one of the most investigated one-dimensional nanostructure in the last few decades owes its popularity to its exceptional optoelectronic properties that can be tailored by controlling the morphology and crystallinity^{4,5,6,7}. The degree of crystallinity achieved and the type of polymorphs present in the TiO₂ nanotubes are the deciding factors in tuning their properties. While the anatase phase is favored for applications such as photo catalysis and dye sensitized solar cells^{8,9}, the rutile phase is suitable for gas sensors and dielectrics¹⁰.

The TiO₂ nanotubes formed by the widely used electrochemical anodization method are amorphous in nature and usually require high annealing temperatures (>500°C) for crystalline transition^{3,11,12}. In light of the fact that anatase TONT are more suitable for majority of applications when

compared to its amorphous form, techniques for achieving conversion from amorphous to crystalline are being widely investigated^{8,9}. In the conventional thermal annealing and hydrothermal process, crystallization is achieved at the expense of very high thermal energy budget. Further, such post-fabrication heat treatments create some performance barriers in device applications such as formation of cracks and thin rutile layer at the bottom of the nanotube. This results in poor electronic properties by creating obstacles in carrier pathways and slowing down of the electrons^{13,14}. Moreover heat treatments are not desirable when nanotube arrays are used in applications which involve polymer substrates. These limitations of conventional crystallization at elevated temperatures have led the researchers to study the possibility of room temperature crystallization. Few recent reports of success in this area are by (i) water incubation of nanotubes^{15,16,17} (ii) hot water treatment¹⁸ and (iii) water vapor-assisted crystallization¹⁹. While these are desirable methods for low temperature amorphous-crystalline transformation, the first one has the disadvantage of very long period of water incubation time (>48 hrs.), the second one has very slow rate of crystallization even with hot water at temperature near 100°C and the third method exhibits very poor crystallinity. It is also reported that long time water incubations and water vapor treatment results in the loss of nanotube structure, as they get converted to nanorods or nanowires^{15,19}.

In this communication, we explore a new method for rapid crystallization of TiO₂ nanotubes at room temperature (~25°C), which is superior to all the reported methods till date in terms of crystallization rate. The rapid conversion of the amorphous to anatase phase is successfully achieved at room temperature within a record time of ~ 5 to 15 minutes by applying alternating voltage square pulses to the TiO₂ nanotubes in water, a very efficient method which guarantees excellent reproducibility being attempted for the first time.

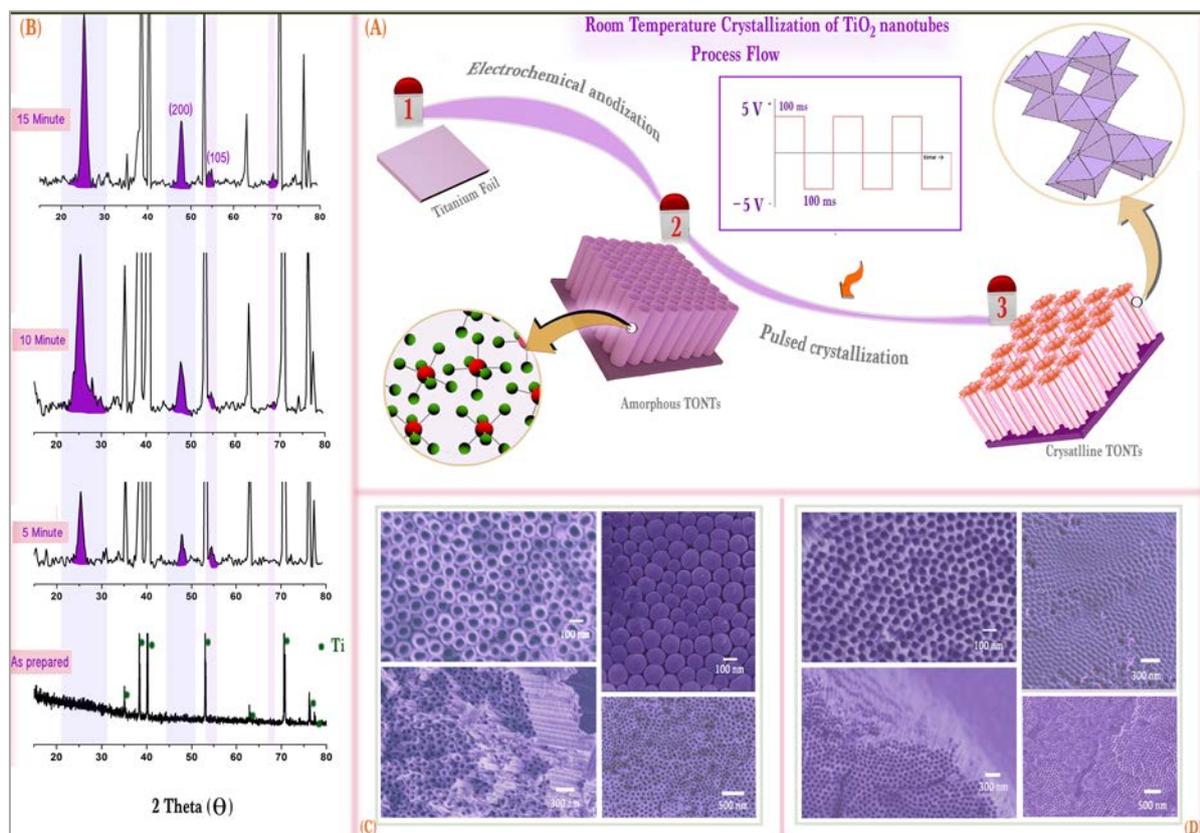


Figure 1 (A) Schematic representation of the formation of TONTs at room temperature. (B) The X ray Diffraction images of the as prepared amorphous TONTs and pulsed crystallized TONTs (C) FESEM false colored images of as prepared TONTs (D) FESEM false colored images of the pulsed crystallized TONTs.

A schematic representation of the process flow of amorphous to crystalline transition is given in Figure 1(A) the room temperature crystallization is done by a two-step method. In the first stage, self-organized and well aligned TiO₂ nanotubes are fabricated via electrochemical anodization of the titanium foil in ethylene glycol fluoride containing electrolyte^{20,21}. The as fabricated amorphous TONTs are converted to the anatase crystalline nanotubes by applying alternating square pulses in the second stage. Square pulses of 5V are supplied alternatively to the TONT tubes placed in a solution of 1 M KCl in distilled water. Here, platinum foil is used as the counter electrode in the process.

The X-ray diffraction spectra (XRD) taken at various stages of formation using a Bruker D8 advance X- ray diffractometer clearly suggest that as formed TONTs are amorphous and that appreciably good crystalline TONTs are formed within the first five minutes of pulse treatment and very high crystallinity is

achieved within 15 minutes (Figure 1(B)). This indicates a rapid phase conversion from amorphous to anatase due to the application of the alternating voltage square pulses. The XRD reveals the anatase crystallites to be prominently oriented along the [101] direction even with increase in the treatment duration. Other peaks appearing are (200) and (105) of the anatase TONT. The surface morphology of the tubes are studied using a Carl Zeiss Sigma Field Emission Scanning Electron Microscope (FESEM). The FESEM images (Figure 1(C)) reveal the perfect tubular structure of the amorphous and crystalline TONTs. The aspect ratio before and after room temperature crystallization is 100 and 86 respectively. It is noteworthy that the tubular structure is maintained intact after the pulsed crystallization here, whereas room temperature crystallization by water incubation and water vapour treatments are reported to result in the destruction of the nanotube morphology^{15,19}

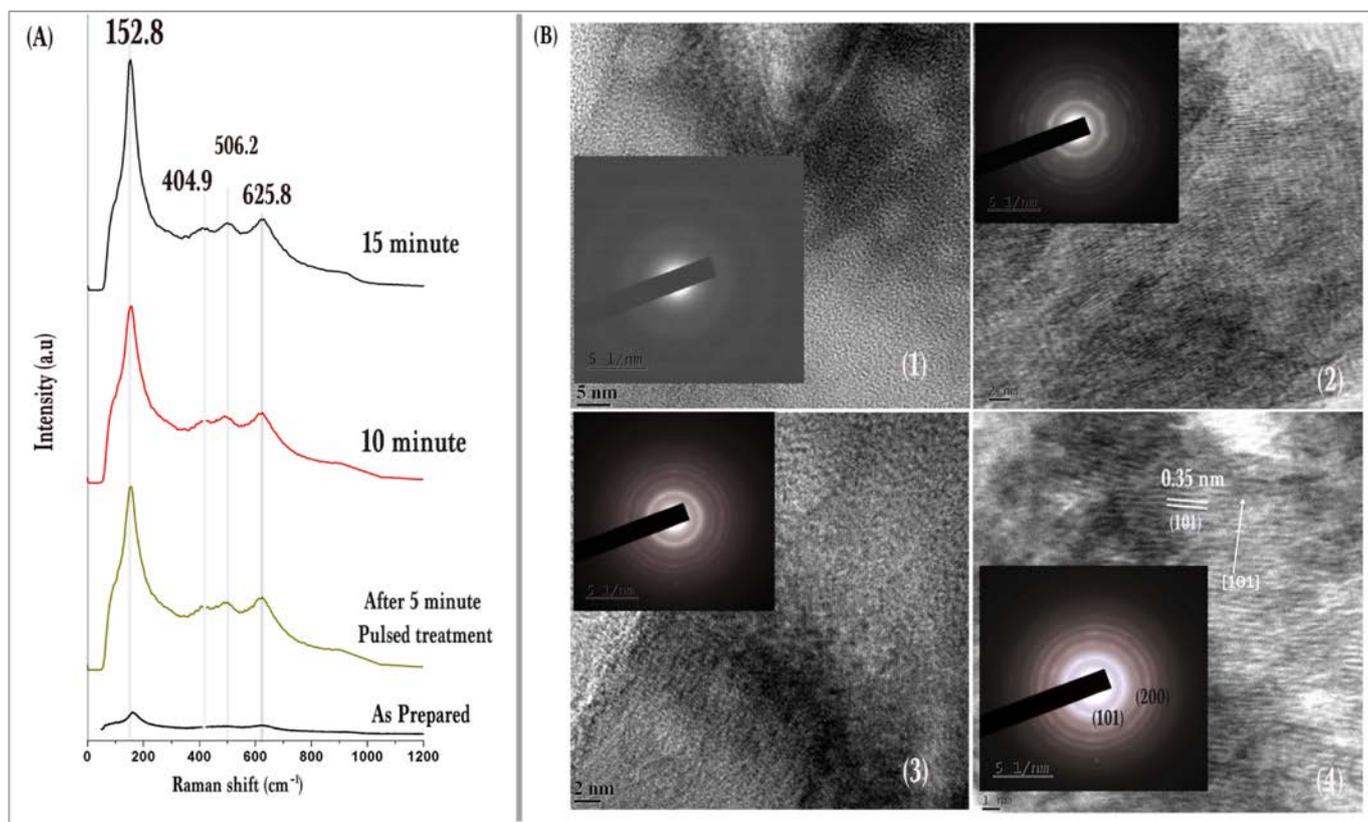


Figure 2 (A) Raman Spectroscopy of the pulsed crystallized TONT at various treatment times (B).TEM images of the as prepared TONT (Figure 2B.(1)) and TONTs, Pulsed crystallized for 5 min (Figure 2B.(2)) , 10 min (Figure 2B.(3)) and 15 min(Figure 2B.(4)).

The ultrafast crystallization and phase purity of the tubes are further confirmed by Raman Spectroscopy and Transmission Electron Microscopy. Raman spectra of the samples are collected using Witec Alpha 300 RA (Nd- Yag) 532nm. The Raman spectra shown in Figure 2(A) reveal four peaks around wave numbers 152.8, 404.9, 506.2 and 625.8 cm^{-1} with the peak at 152.8 cm^{-1} possessing the strongest intensity. The anatase TONT belongs to phase group D_{4h}^{19} and is reported to have six bulk lattice vibrations at 144, 197, 399, 513, 519, 639 cm^{-1} corresponding to E_g , E_g , B_{1g} , A_{1g} , B_{1g} and E_g respectively²². The broadening and frequency shift of the peak positions are common in nanocrystals^{22,23}. The peaks obtained here are in close agreement with that reported by Su *et al* for TONTs. No

rutile Raman peaks are observed here thereby confirming the phase purity of the crystallized samples.

The High Resolution Transmission Electron Microscopy (HRTEM) images for the amorphous and crystallized TONTs are depicted in Figure 2(B.1). The planar spacing in the pulsed crystallized TONT is found to be 0.35 nm corresponding to the (101) crystal planes, corroborating the XRD data which indicates predominant orientation of nanocrystallites along (101) planes. The Selected Area Electron Diffraction (SAED) micrographs (Figure 2(B.4)inset) reveal a ring structure indicating polycrystalline TONT formation for all the crystalline samples while, the single spot SAED pattern (Figure 2(B.1) inset) is indicative of the amorphous structure of as-formed TONT.

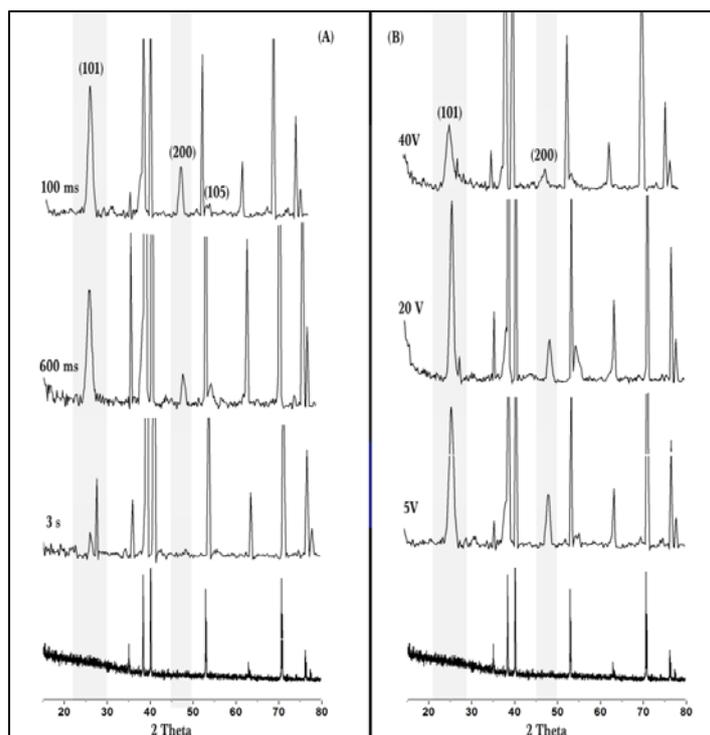


Figure 3. X- ray diffraction pattern (2 theta vs Intensity) to show the dependence of pulse width (Figure 3A) and applied voltage (figure 3B) of alternating square pulses on room temperature crystallization.

In order to understand the dependence of crystallization on pulse width, alternative square pulses are applied at different pulse widths (3 s, 600 ms and 100 ms) to the as prepared TONTs (Figure 3A). The TONTs that are treated with square pulses of pulse width 3 s in conducting water are found to have poor crystallinity. The crystallinity of the TONT starts to increase as the pulse width decreases to 600 ms and the TONTs that are subjected to pulse width 100 ms are observed to exhibit highest crystallinity in the present study. This observation reveals the inverse relationship between the pulsewidth and crystallization. Further the effect of change in voltage on inducing crystallization is studied by varying the voltage applied at room temperature as 5, 20 and 40 V (Figure 3B). The TONTs that are treated with alternative square pulses at 5V and 20V show better crystallinity than at 40V and as the voltage is increased above 5V the TONT layers show a tendency to peel off, thus limiting the optimized applied voltage to lower values.

In the reports on water incubation crystallization method, it is proposed that distributed TiO_6^{2-} octahedra are dissolved in

water and rearrange themselves to precipitate as anatase phase. The dissolution-precipitation process makes the water incubation process a time consuming technique, while in the present work the rapid application of negative pulse followed by the positive pulse induces crystallization at the site without any direct dissolution of TiO_6^{2-} octahedra^{15,16}. The Figure 4 outlines the mechanism proposed for the rapid pulsed crystallization of TONTs by application of alternative voltage square pulses at room temperature. It is widely acknowledged that the basic building blocks of TiO_2 polymorphs are $Ti(OH)_6^{2-}$ octahedra¹⁰ and that the as formed amorphous TONTs have surface hydroxyl groups attached to the TiO_6^{2-} octahedra leading to the formation of distributed $Ti(OH)_6^{2-}$. In the present work, the amorphous to crystalline transition of TONT at room temperature is explained based on an induced electrophilic- nucleophilic reaction. In the first stage of crystallization, a positive pulse (+ 5V) is applied to the amorphous TONTs immersed in water. It turns the amorphous TONT electrode electrophilic and causes accumulation of OH^-

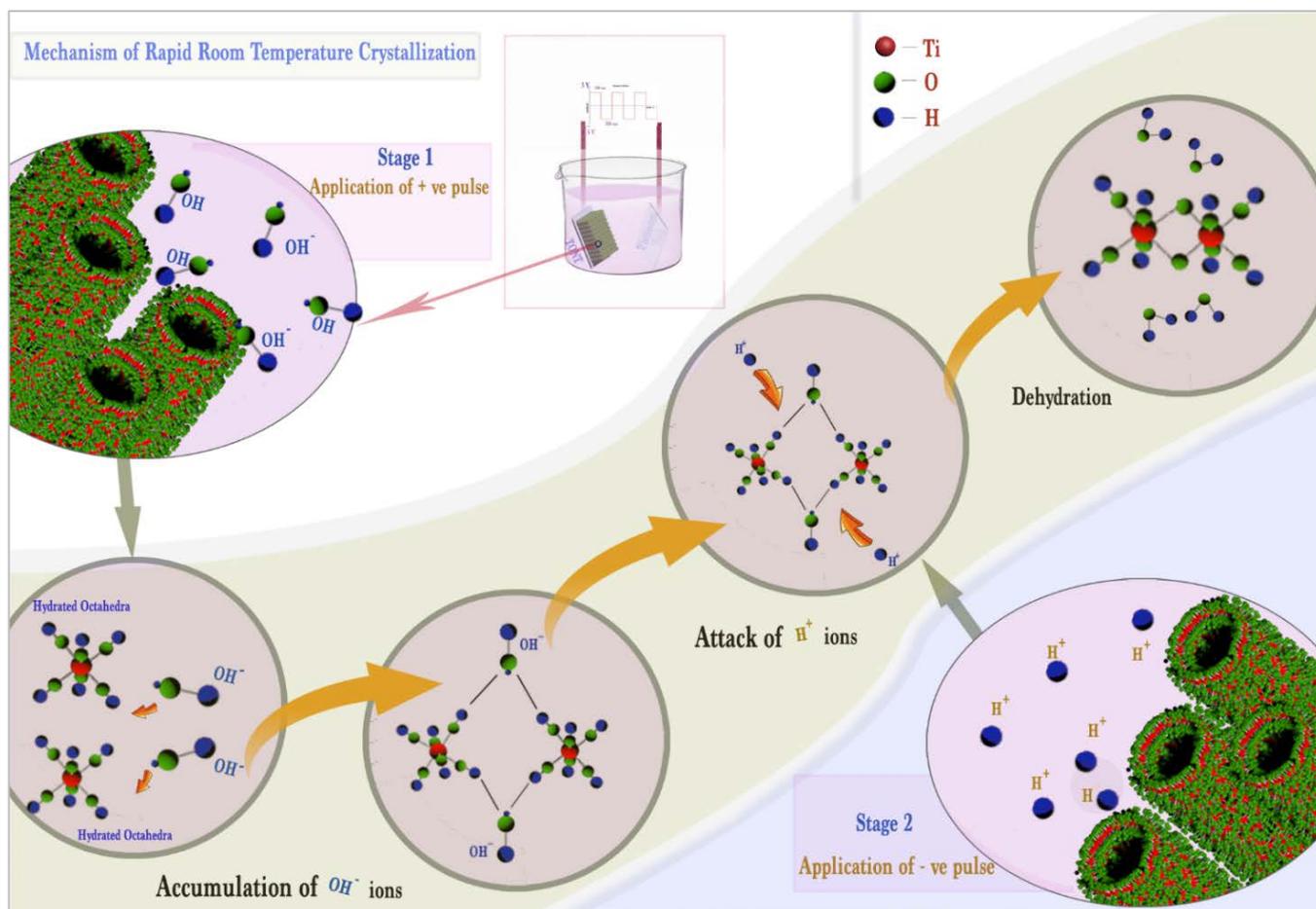


Figure 4. The mechanism of the superfast room temperature crystallization of TONTs.

ions from water over its surface. The lone electron present on these OH^- ions form bridge bonding with the hydroxyl ions present in the two adjacent $\text{Ti}(\text{OH})_6^{2-}$ octahedra of the TONTs. In the second stage which is initiated within the next 100 ms, an alternated voltage supplies a negative pulse (-5 V) to these TONT electrodes making them nucleophilic which causes the attraction of hydrogen ions in water towards the nanotubes. The attack of hydrogen ions triggers the dehydration from the two $\text{Ti}(\text{OH})_6^{2-}$ octahedras of TONT that are bridged by OH^- ions and results in the formation of edge shared octahedras. This process continues until the basic crystal of anatase is formed. This electrophilic-nucleophilic mechanism activated by alternating pulses offers a much faster low temperature TONT crystallization because here the process does not require any actual dissolution of TiO_2^{2-} in water as reported by different researchers^{15,16}.

In conclusion, this pulse induced-superfast room temperature crystallization can be considered superior to the conventional thermal annealing technique owing to its advantages like crystallization at lower thermal budget, very high reproducibility and greater crystallization rate. Moreover this method can be generalized to the fabrication of different

crystalline TiO_2 nanostructures such as nanorods, nanopowder and thin films.

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