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Nanotube Formation And Surface Evolution On Hydrothermally Treated Ti In Alkali Solution

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Abstract. The present study intends to check which nanotube formation mechanism match the surface evolution on bulk Ti surface after soaked in hydrothermal treatment. Polished cp-Ti disks were hydrothermally immersed in various concentration NaOH for 1h, 2h, and 4h at 220°C. The SEM observations and XRD studies showed a sequence transformation from polished Ti surface into titanium oxide with plate shape and leave-like structure in the beginning. Bigger plates or leaves oxide then evolved into sodium titanate nanorods that finally became nanotubes as the immersing time lengthened. Apparently self-assembly and partial dissolution were the most applied mechanism to explained the sodium titanate formation. Plate and leaves-like oxide mainly formed by dissolution of Ti metal followed by precipitation of TiO_6 in self-assemble manner as the resultant of reaction between $Ti(OH)_3^+$ and OH^- . While, nanorod and nanotube structure were produced by partial dissolution of leaves structure followed precipitation of sodium titanate by reaction of Na^+ with $HTiO_3^-$ generated from OH^- reaction with Ti metal and TiO_6 .

Keywords: sodium titanate nanotube, hydrothermal, formation mechanism, dissolution-precipitation, self-assembly

1. Introduction

Titanate nanotube is widely known for its electrical properties which extensively applied in various application such as semiconductor[1][2] and photocatalysis[3] due to its high amount of surface area and superior physico-chemical properties. When titanate is synthesized via single step hydrothermal route in NaOH without calcining, ion exchange or HCl washing, sodium titanate can be generated [4][5]. In medicine applications, sodium titanate layer has been reported as bioactive layer due to its ion exchangeable surface making bone-like apatite deposited easily during immersion in SBF (simulated body fluid) solution [6][7]. Other studies also found that nanowire and nanofiber sodium titanate could form a self-assembly scaffold that is expected to allow living tissues to have ingrowth access [8]. These previous studies mentioned suggested nanostructure titanate as a potential coating layer in biomaterial especially hard-tissue application. Sodium titanate nanotube also performs anti-bacterial properties by performing novel photocatalysis



reaction that can reduce the number of *Staphylococcus aureus* [7] (with or without UV radiation) and *Escherichia coli* [9] under UV radiation.

Despite its broad potential application, discussion over the formation mechanism of titanate nanotube is still being explored ever since the first time titanate nanotube was synthesized via hydrothermal treatment by Kasuga in 1998[10]. There are couple acknowledge formation mechanisms proposed in explaining nanotube formation without template-assisted. First postulate is rolling mechanism which explains that nanotubes are formed by rolled nano-sheets in the continuation of sheets exfoliation from the precursor [11]-[15]. The second statement is self-assembly which involving dissolution and precipitation process. Dissolution of outer parts of precursor occur as reaction with active component of basic solution, until precipitation begins, the structure will assemble accordingly to form nanotube [16][17]. Rolling mechanism can technically explain the process nanotube development synthesized from powder precursors. Yet, for non-powder precursor, it tends to be difficult to elaborate delaminating and scrolling process in structure development. Both rolling and self-assembly mechanisms involve ion exchange step in nanotube formation, which studies found that nanotube will not be generated without acid washing step [18]. Apparently, nanotube can still be generated in single step hydrothermal treatment only the nanotube has sodium in titanate compound [4][5]. Regarding to this, another formation mechanism were proposed by Wenjun D. et al. hypothetically explain sodium titanate nanotube formation on the surface of titanium mesh, which Wenjun D. presented upward-downward mechanism that involving co-mechanism between corrosion and self-assembly. Nanotube structure grows upward at the tip nanowire by self-assembly whilst nanowire vertically keeps growing downward on corrosion region [7].

Each mechanism brought up such a supportive evidence; therefore further experiments are needed to verify the empirical value of proposed mechanism. The present study successfully synthesizing sodium titanate nanotube on bulk titanium disk surface via single step hydrothermal treatment. Sodium nanotubes were obtained through single alkali treatment without ion exchange or acid washing precursor. By observing morphology evolution, this study intends to predict the chronological reactions and to configure which formation mechanism fits.

2. Materials and Methods

Sample preparation

C.p. Ti disks grade 2 with diameter 15 mm and thickness 2 mm were polished on SiC paper #400, #800, #1200, and #2000 in sequence. Polished c.p Ti disks were ultrasonicated in acetone, ethanol, and distilled water for 20 minutes each then hydrothermally immersed in three different concentrations of NaOH; 0.5M, 1M and 2M at 220°C, for 1h,2h and 4h. Hydrothermal treatment was carried out in stainless steel-Teflon line vessel where four disks were immersed in 10mL of NaOH solution. After treatment the disks were sonicated in distilled water for 15 minutes and dried in room temperature.

Characterizations

Chemical compound on the surface of the samples was examined by X-Ray Diffractometer for thin films, MPD-Pro. PANalytical Co. Ltd., Germany (Cu K α , $\lambda = 1.5418 \text{ \AA}$) scanned form 20° to 70° (2 θ). While surface morphology and elemental composition were characterized using field emission type scanning electron microscope (FE-SEM) S-4800, Hitachi Co., Japan equipped with energy dispersive X-ray spectroscopy (EDS) and field emission type transmission electron microscope (FE-TEM) Tecnai G2 F20 S-TWIN. IR study was also carried out to observe the

hydroxyl (OH) group on nanotubes structure using Thermo Scientific Smart iTR Nicolet iS10 from wavelength 570- 4000 cm^{-1} in reflectance mode.

3. Results and Discussion

Morphology and composition studies

Various morphologies on Ti surface after treated in NaOH at 220°C can be observed in Table 1. After 1h immersed in 0.5 M, a uniform plates structure formed on Ti surface which the structure grew bigger and turned into a leaves-like shape on several places when immersion time increase into 2h. After 4h the leaves-like structure dominates with some rod and short wire structures appeared in between. Samples treated in 1M concentration for the morphology appeared relatively similar with samples immersed in 0.5M, only leaves-like structure formed early after 2h. Leaves structure completely changed into rod or short wire shape after 4h. While samples immersed in 2M NaOH show leaves-like structure appeared just after 1h and transformed into rod structure after 2h. After 4h immersed in 2M concentration, the rod structure grow longer into nanowire structure with the diameter of wire around 25 nm – 50 nm. Further observation on nanowire by TEM imaging in Fig. 1 shows that nanowires are happened to be multilayer nanotubes with lateral growth direction and wall thickness about 5-10 nm. XRD analysis in Fig. 2 showed only octahedral oxide peaks when plate-like or leaves-like structure appeared. As rod structure appeared in between leaves structure, sodium titanate peaks were detected with stronger intensity as immersion time gets longer. Although the morphology completely turns into randomly arranged nanotubes on samples treated in 2M concentration for 4h, octahedral oxide peaks still showed along with sodium titanate strong peaks.

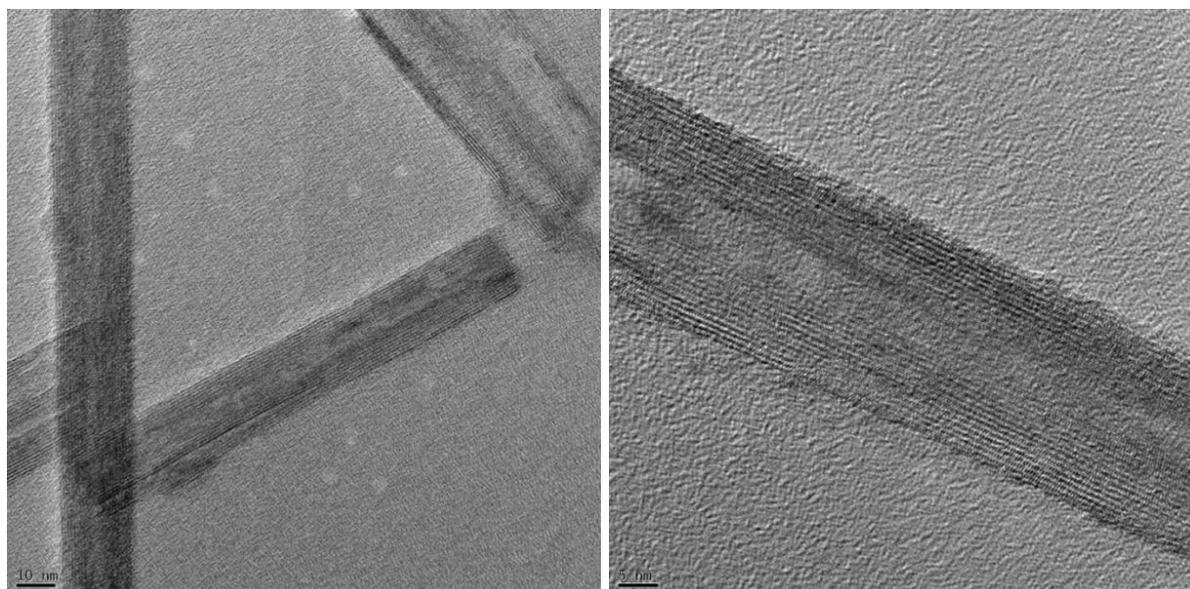


Fig. 1. TEM observation revealed the nanowires on sample treated in 2M concentration for 4h are nanotubes

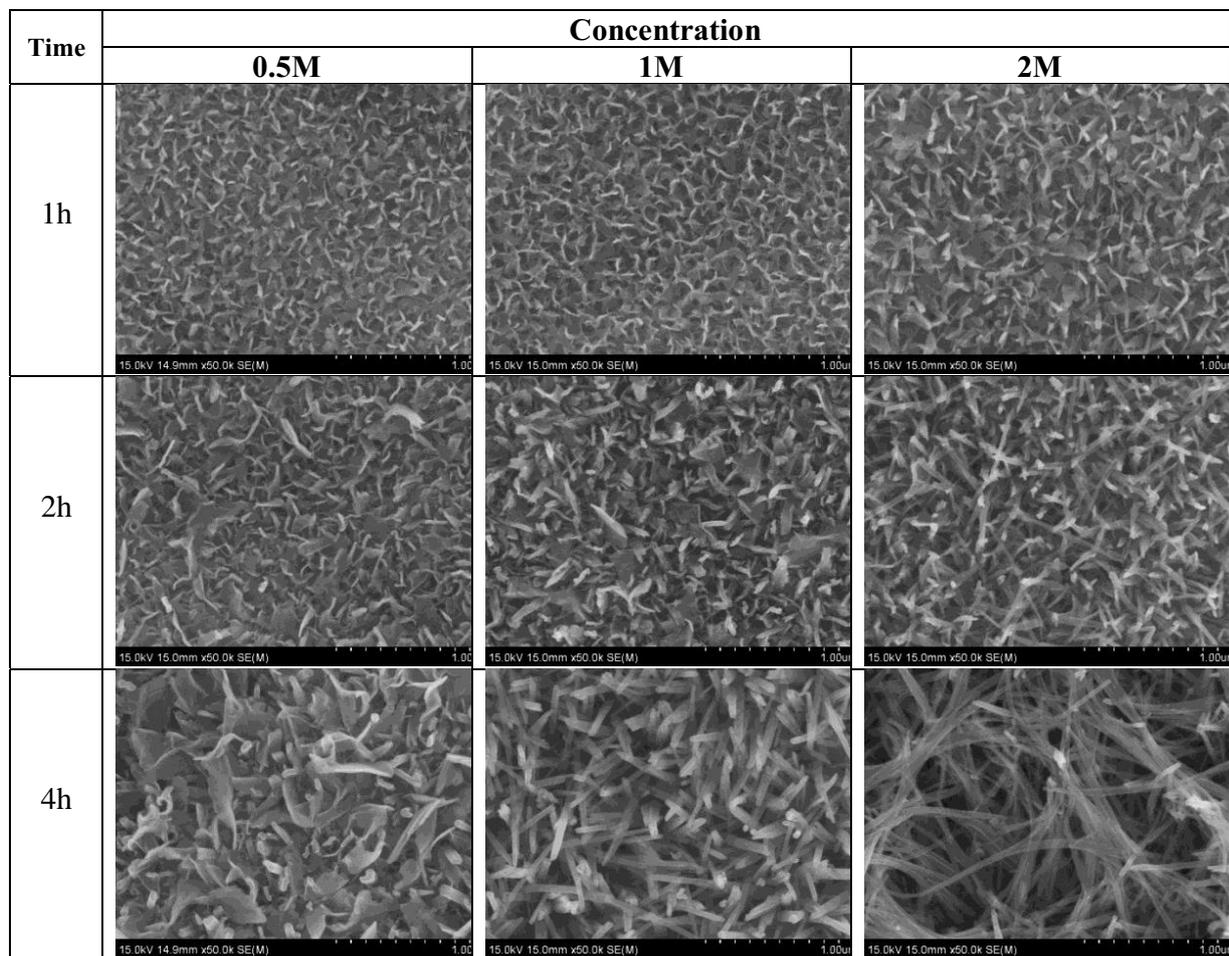


Table 1. SEM observation of NaOH treated samples at 220°C with various concentration and immersion time

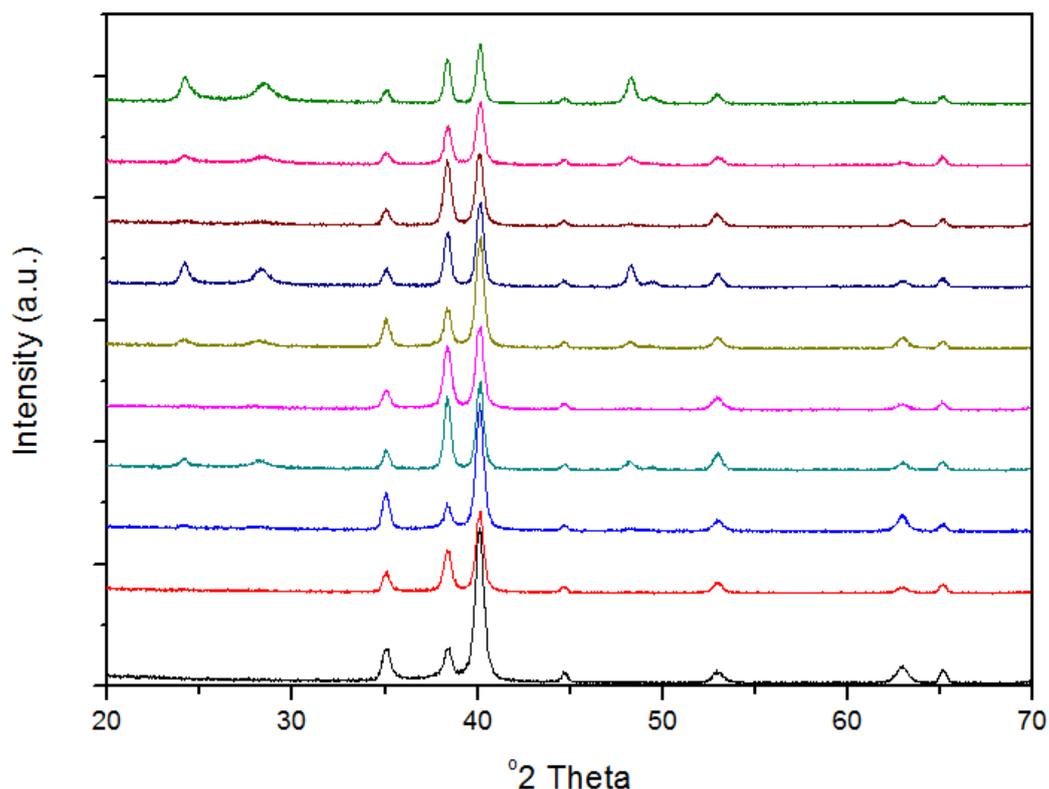


Fig 2. XRD pattern of NaOH treated samples with various concentration and immersion time treated at 220°C

Hydrothermal reaction and structure formation

SEM observation of morphology evolution on the present work cannot strongly support the rolling mechanism. In rolling mechanism the exfoliation and roll process were logically accepted when the precursors utilized is powder, yet to have the plate or leaves-like structure exfoliate or peel off from the disk to rolled up and then re-attach to disk is unmatched explanation for the morphologies observed in Table 1. While, upward and downward mechanism seems more acceptable in explaining how the rod shape grows into long wire and nanotubes formed by self-assembly. However, upward and downward mechanism does not completely satisfy explanation how the plate and leaves-like structure appeared and disappeared during the observation.

Under hydrothermal condition there are some different expectations of reaction type reported [15] such as; Decomposition, dissolution, corrosion, etching; Crystal growth of inorganic compounds; Synthesis of new phases; Leaching of ores in metal extraction; Preparation of microcrystallites with well-defined sized and morphology for specific application. By assuming that either the plate structure or nanotubes formation follows self-assemble mechanism means there are several dissolution and precipitation processes involved as illustrated in Fig. 3. The present study proposed partially dissolve mechanism on sodium titanate nanotube formation. The mechanism consists of two stages of dissolution and precipitation processes.

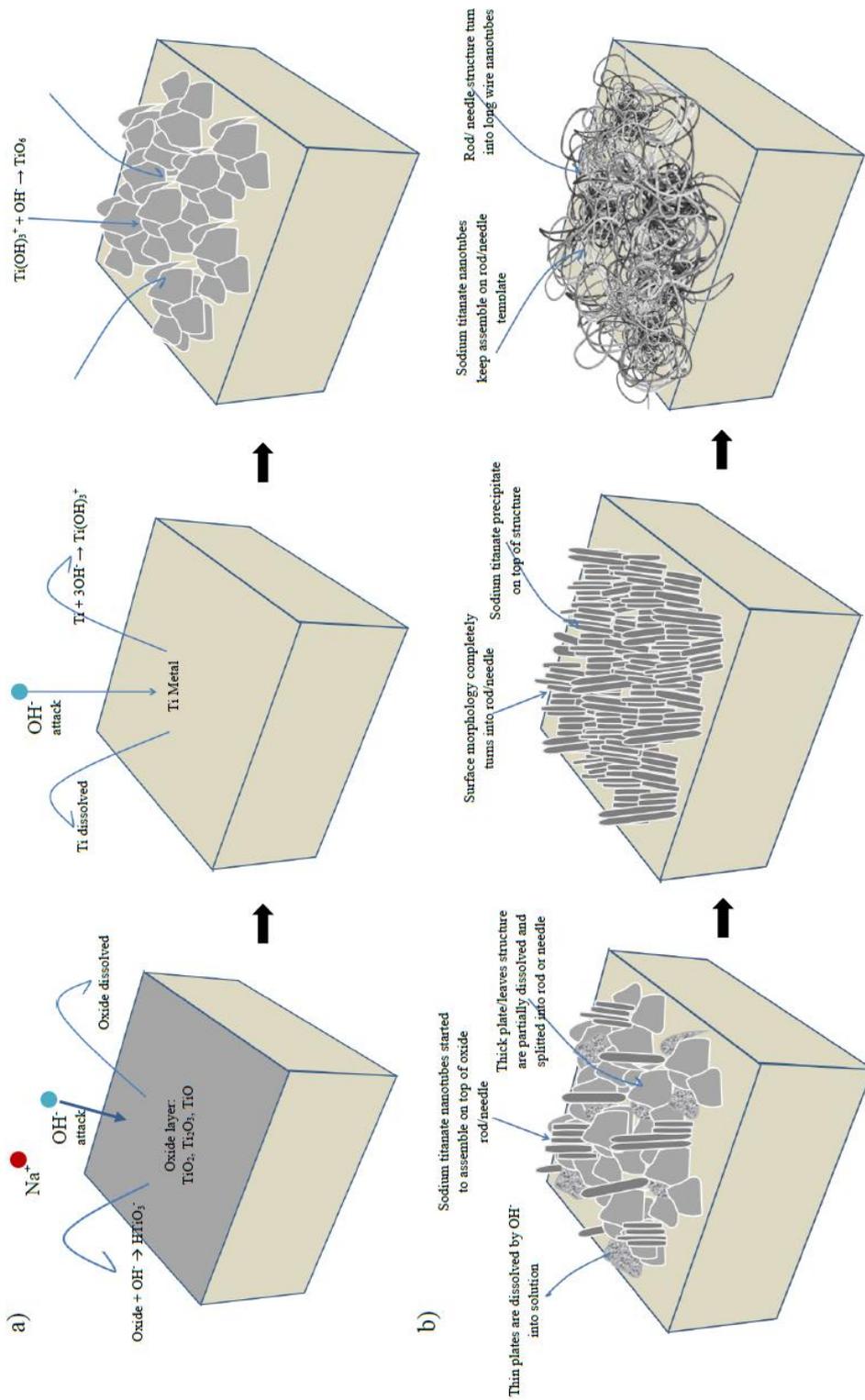
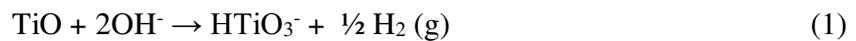


Fig. 3. Illustration of partially-dissolved mechanism consists if; a) octahedral oxide formation, produces plates to leaves-like structure; b) sodium titanate formation, involves partial dissolve and splitting process

The first dissolution-precipitation produces fine plate octahedral oxide that continuously grows into leaves-like structure. The plate structure formation most probably started with the dissolution of the thin passive oxide layers (TiO, TiO₂ and Ti₂O₃) on Ti by the corrosive attack of hydroxyl group (OH⁻). Hydrogen metatitanate (HTiO₃⁻) from Eq. 1-3 reacted with sodium ion could form sodium titanate (Na_xTi_yO_z) deposit (Eq. 8), yet sodium titanate nanotubes were still not precipitated in this stage due to the small amount of passive oxide layer. Studies on titanium oxides [16][17] confirmed that after one day of exposure to air the oxide thickness reach up to 3.17 nm, this amount was probably not enough to initiate precipitation in the first stage of dissolution-precipitation process.



After the passive layers were done, the hydroxyl group will attack Ti metal and formed Ti hydroxide ion (Eq. 4). The precipitation started to occur once hydroxide ion (Ti(OH)₃⁺) that react with hydroxyl group produced titanium octahedral oxide (TiO₆) (Eq. 5) and quickly reached supersaturated point.

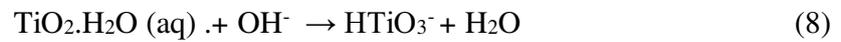
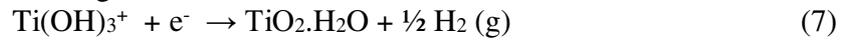


In second stage both of octahedral oxides with the plate and rod structure exist on titanium surface. In this point these structures might compete for their existence to grow. Since thermodynamically plate and leaves-like structure are less stable than needle and rod structure, they tend to dissolve or transform. Fig. 4 showed some rods appeared in between of various thicknesses plate structure. The plates with enough thickness will probably splitting into rods while the thin one will partially dissolve by hydroxide into hydrogen metatitanate. After the partial-dissolve process happened, octahedral plate and leaves structure disappeared left the needle or rod structure completely dominated Ti surface. Rod or needle structure itself seems to be the template for nanotubes to assemble in this case.



Sodium titanate precipitation process relates to the continuation of Eq.4. Before sodium titanate started to assemble on the top of rod or needle structure, titanium dioxide hydrate with hydrogen gas formed first. The pressure generated by H₂ gas could be one of the hindrance factors why the oxide hydrate was not precipitate. Instead of precipitating, titanium dioxide reacted with hydroxide producing hydrogen metatitanate. Further reaction between hydrogen metatitanate and sodium ion (Na⁺) generated sodium titanate. Hydrogen metatitanate generated from both partial-dissolves process and dissolution of oxide hydrate produced the self assemble sodium titanate nanotube on the top of rod/needle structure. Partial-dissolves process also explains the existence of the octahedral oxide peaks when plate structure disappeared and titanium surface fully covered with

of nanotubes. The octahedral oxide plates were only dissolved partially with some part of them transform into template for nanotubes growth.



Eq. 9 implied that sodium titanate nanotubes were associated with hydroxyl group in final product. IR spectra on Fig. 5 showed OH broad peak from wave number 3100 to 3600 cm^{-1} with the maximum percent reflectance at 3400 cm^{-1} . Another OH group vibration also appeared at 1623 cm^{-1} on the surface of titanate nanotubes, this peak is identified as molecular water bending [18].

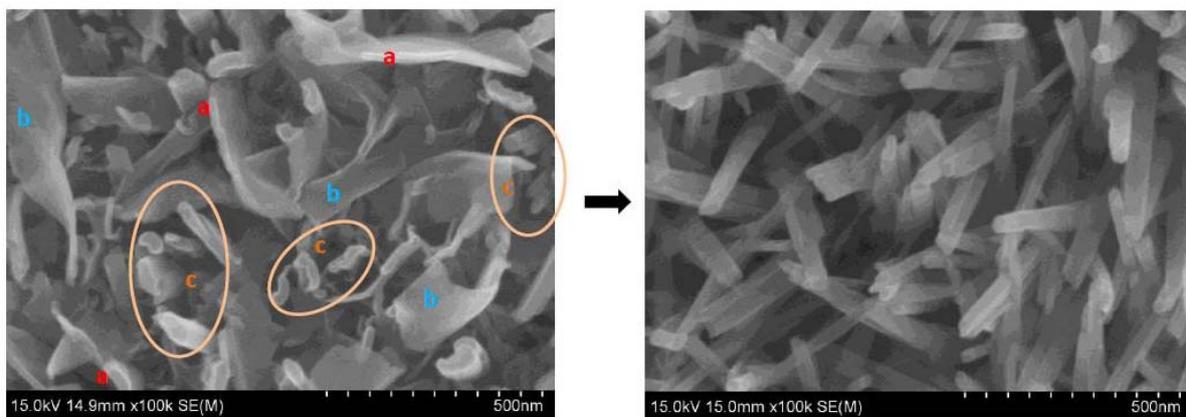


Fig 4. Transformation from plate/leaves-like structure to rod/needle structure involves partial dissolves process a) some thick plate or leaf structures split into rod b) the thin plates or leaves that is potentially disappeared c) splinted rod

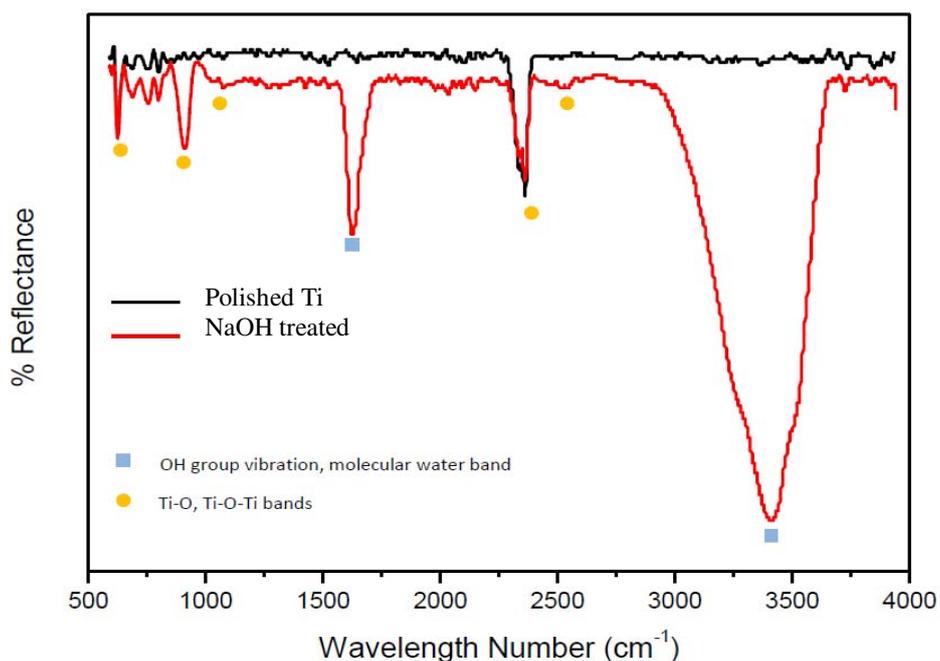


Fig. 5. IR reflectant spectra of polished Ti and sodium titanate nanotubes in wave number range from 570 to 400

4. Conclusions

Self-assembly with two stages dissolution and precipitation process is the most suitable in explaining the sodium titanate nanotube formation. The process is started with octahedral oxide plate structure formation, followed by the octahedral oxide plate partially-dissolve and annihilation then ended up with sodium titanate nanotube self-assembly with the oxide rod/needle as template. However, predicted reactions were purely based on morphology observation and elemental studies therefore further works are needed to confirm.

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