

Electronic Supporting Information (ESI)

Rutile Nanotubes by Electrochemical Anodization

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Electrochemical anodization:

Ti foil of 1 cm x 1 cm (1mm thickness) was polished with fine emery sheet (200 grade). The polished sheet was cleaned by sonication for 15 mins in deionized water, ethanol, iso-propanol and acetone sequentially to remove the impurities on the surface. Anodization was performed in an electrochemical bath at 30 °C controlled by a thermostat. Ti sheet was used as anode and Pt mesh (2.5 x 2.5 cm) was used as cathode. Experiments were performed at anodization potential of 20 V. The anodization was carried out till complete dissolution of Ti foil and nanotubes were collected from the electrolyte solution for drying.

The morphological characterization was done using Scanning Electron Microscopy (SEM), Hitachi FE S4800 and Transmission Electron Microscopy (TEM), Technai 20G² at an accelerating voltage of 200 kV. TEM sample preparation:- suspension of 0.5 mg TiNT powder in 1 ml methanol by sonication followed by its dispersion on carbon coated Cu grid.

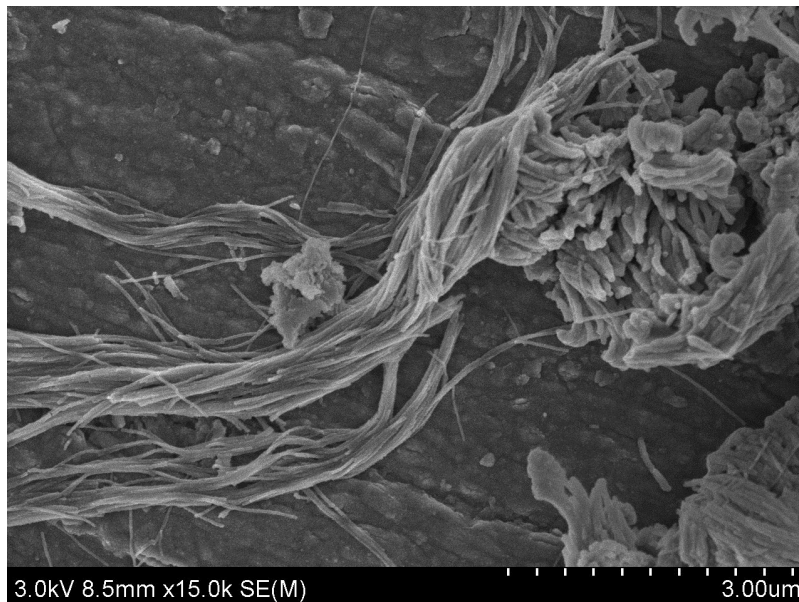


Figure S1: SEM image showing breakdown of bundled nanotubes from the metal surface because of sudden volume expansion.

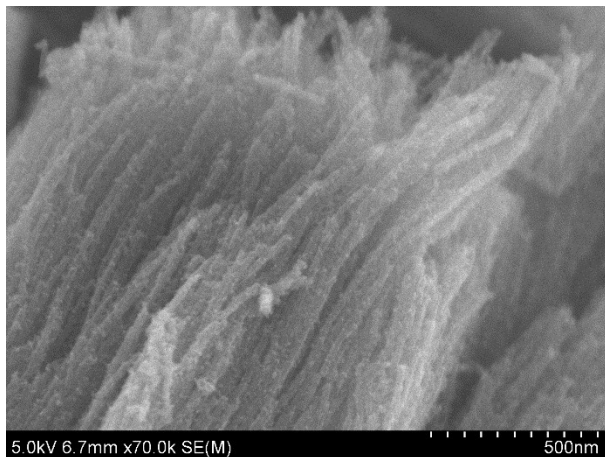


Figure S2: SEM image of TiNT.

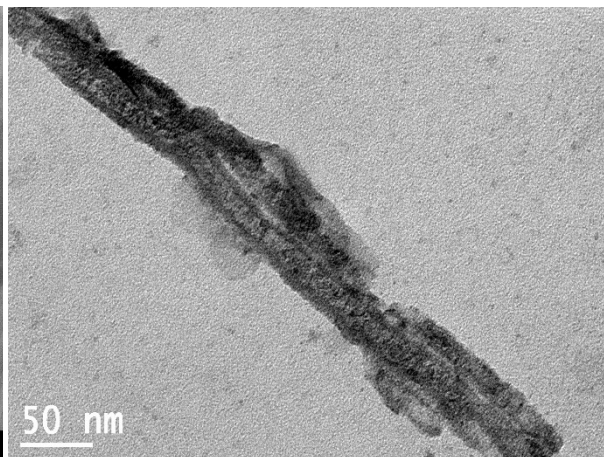


Figure S3: TEM image of TiNT.

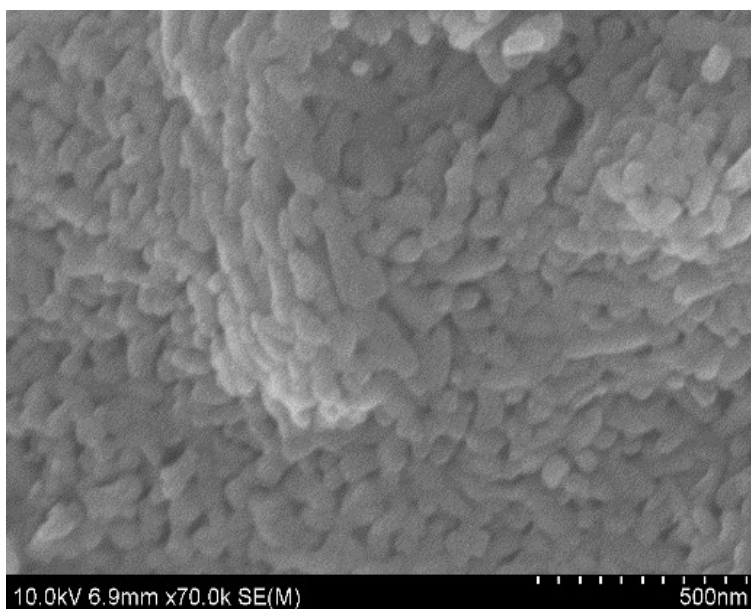


Figure S4: SEM image of distorted nanotubes calcined at 600 °C.

Thermal annealing:

The as formed nanotubes were amorphous and thermal annealing at different temperatures resulted in crystalline phase. Tubular furnace was employed for calcinations at a heating rate of $3^{\circ}\text{C min}^{-1}$. The samples were maintained at corresponding temperature for 3 hours in atmospheric air. Bruker Discover 8 diffractometer with Cu- α radiation of wavelength 1.54 nm, at potential of 20 kV and current value of 30 mA was used to study the XRD pattern.

Raman spectrum was observed from Bruker RFS Raman spectroscopy with laser source of 1064 nm and resolution at 2 cm^{-1} .

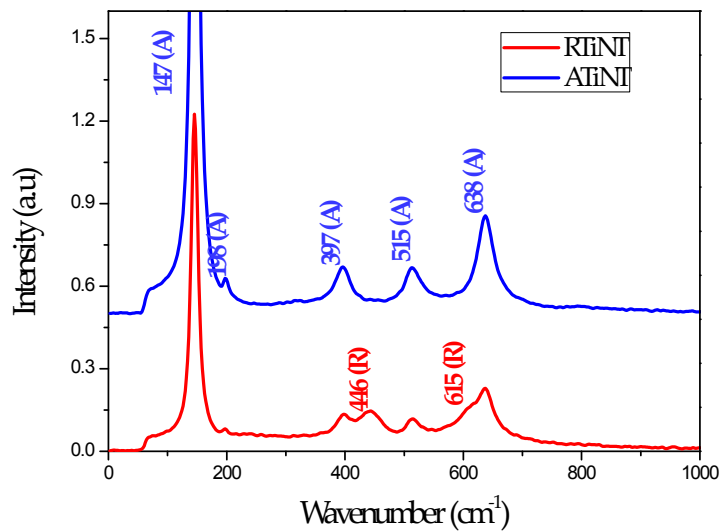


Figure S5: Raman spectrum of A-TiNT and R-TiNT.

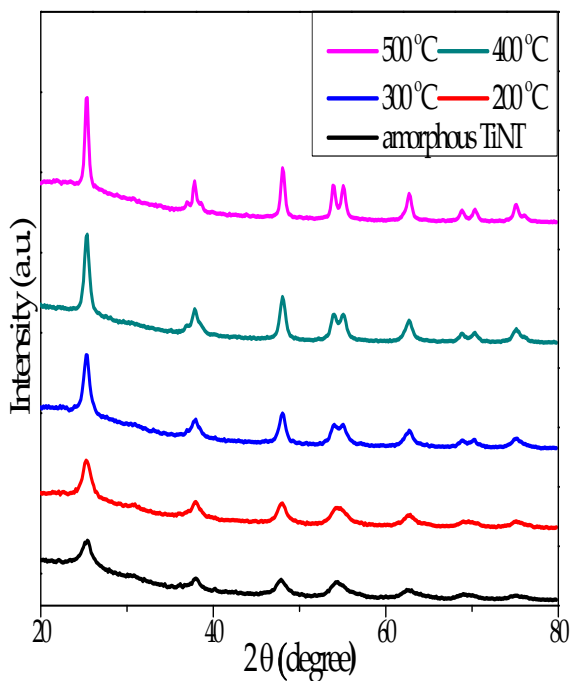


Figure S6: XRD plot of TiNT calcined at different temperature, showing increasing anatase phase with respect to temperature up to 500 °C.

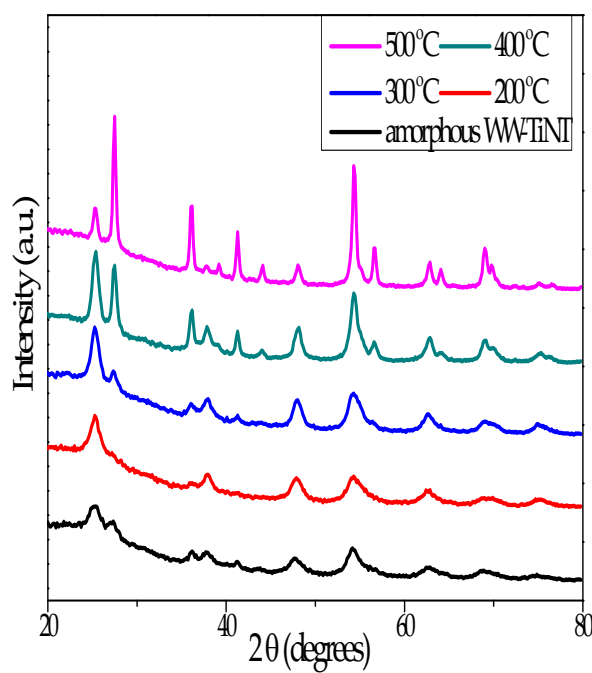


Figure S7: XRD plot of WW-TiNT calcined at different temperature, showing preferential increase in rutile phase with respect to temperature.

Effect of acid treatment over crystallinity:

The samples were stirred in corresponding acid solution for 1 hour and allowed to settle, the settled NT were dried after removing supernatant solution. The dried samples were annealed at 500°C.

In case of HCl treatment, heat treatment at 500 °C yielded 36 % of rutile phase. Sample treated with 300 mM acid concentration resulted in 60 % rutile phase after annealing at 500 °C (**Figure S8**). However, SEM showed completely distorted of NT morphology with 300 mM concentration.

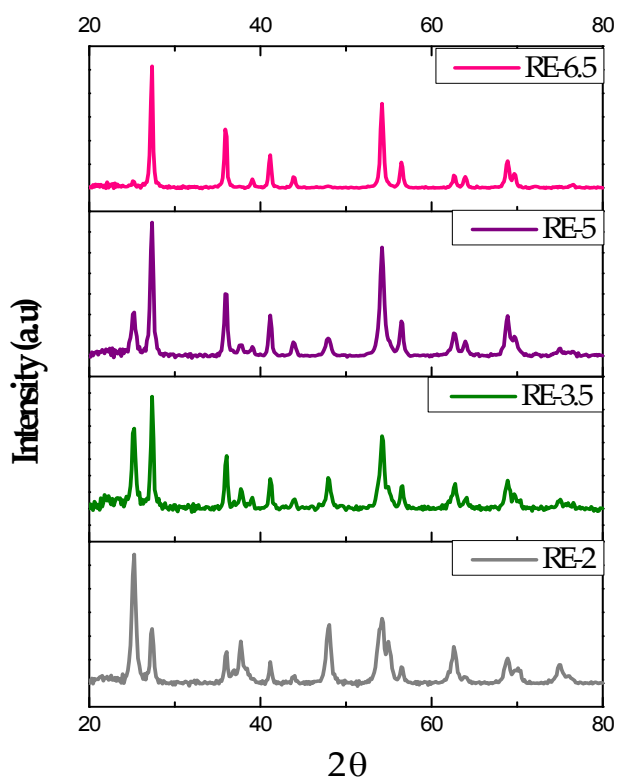


Figure S8: XRD plot of 500°C calcined WW-TiNT dried with different amount of residual electrolyte.

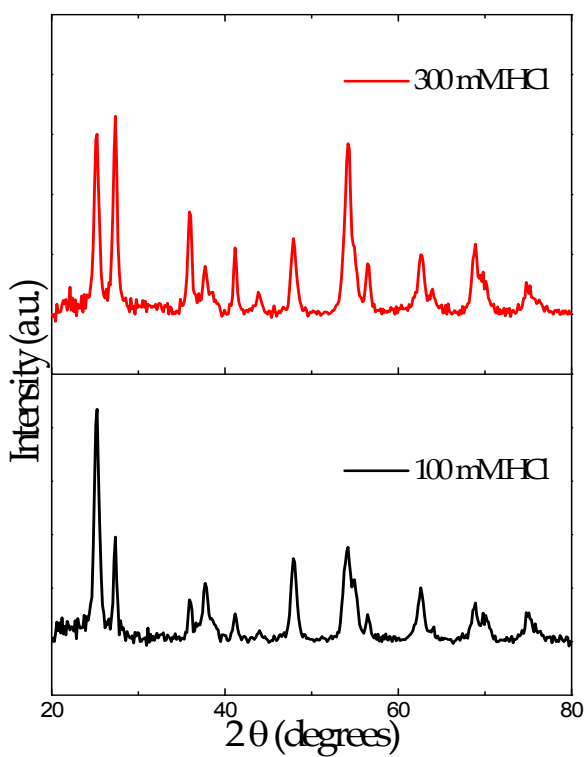


Figure S9: XRD plot of 500°C calcined TiNT, treated with two different HCl acid concentrations.

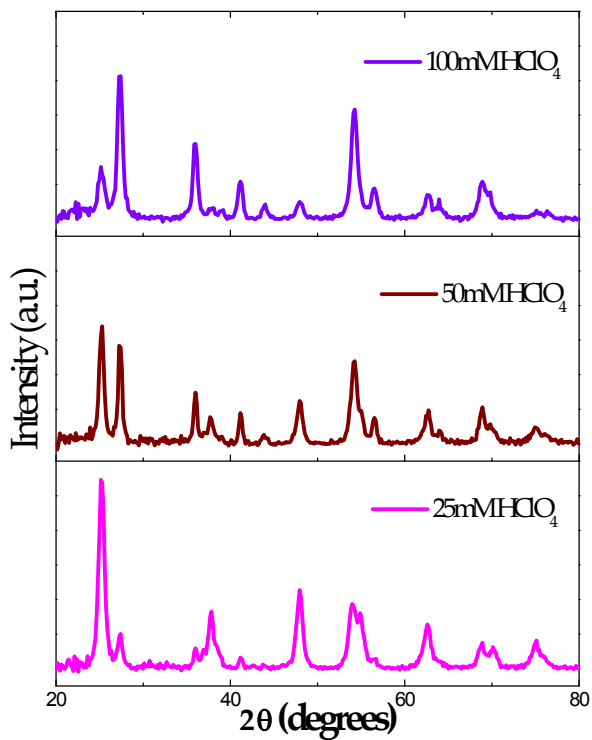


Figure S10: XRD plot of 500°C calcined TiNT, showing increasing rutile phase formation with increasing chloride ion (HClO_4) concentration.

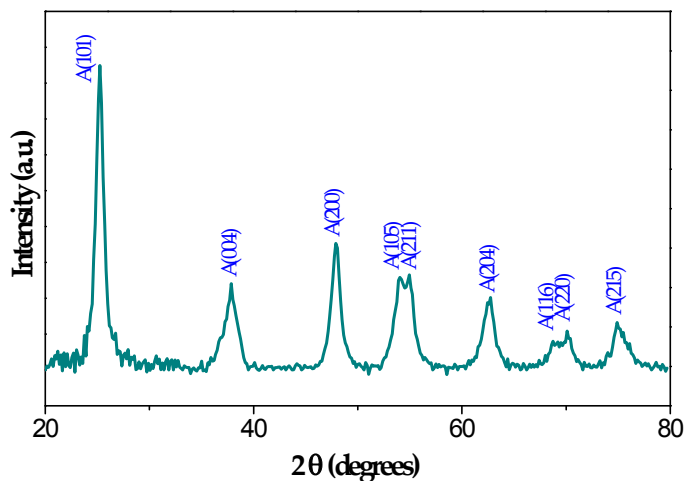


Figure S11: XRD plot of 500°C calcined TiNT, treated with 100 mM H_2SO_4 showing pure anatase phase.

EDX results for different residual electrolyte volume:

WW-TiNT was dried with different amount of residual electrolyte solution, EDX measurement of the dried amorphous samples showed decrease in oxygen concentration with increasing residual electrolyte (RE) volume.

Table S1: Elemental composition (wt. %) of titania nanotubes samples dried with different volume of residual electrolyte.

Element	2 ml RE	3.5 ml RE	5 ml RE	6.5 ml RE
O	60.37	45.97	45.64	23.45
Cl	4.83	5.84	6.38	6.35
Ti	34.80	48.19	47.98	70.20

Phase ratio calculation:

Weight ratio or phase ratio for anatase and rutile was calculated based on Spurr Myer's equation (Equation 1 and 2).

$$W_A = \frac{1}{1 + 1.26 \left(\frac{I_R}{I_A} \right)} \quad (1)$$

$$W_R = 1 - W_A \quad (2)$$

W_A and W_R represents anatase and rutile weightage, multiplying by 100 gives corresponding percentage phase ratio. I_R and I_A are the maximum observable peak intensities, here for all the samples peak intensity of anatase 101 plane at 25.2° (2θ) and rutile 110 plane at 27.3° (2θ) was used.

Optical property by UV DRS:

Diffusive reflectance spectroscopy (ThermoScientific, Evolution 600) showed the absorbance spectrum of heat treated (500°C) TiO_2 powder samples (Error! Reference source not found.S12). This spectrum can be used to predict bandgap by using energy graph (Absorbance Vs. energy (E) in eV). Wavelength (λ) is converted to energy using equation 3.

$$E = \frac{hc}{\lambda} \quad (3)$$

Where, $h \rightarrow$ Plank's constant (6.626×10^{-34} J m)

$c \rightarrow$ Velocity of light (2.998×10^8 m/s)

$1 \text{ eV} \rightarrow 1.602 \times 10^{-19}$ J

The calculated bandgap for TiNT was found to be 3.102 eV which is near to the commercial catalyst Degussa-P25 (3.107 eV), the R-TiNT showed red shift with bandgap value of 2.99 eV indicating the visible activity of R-TiNT catalyst.

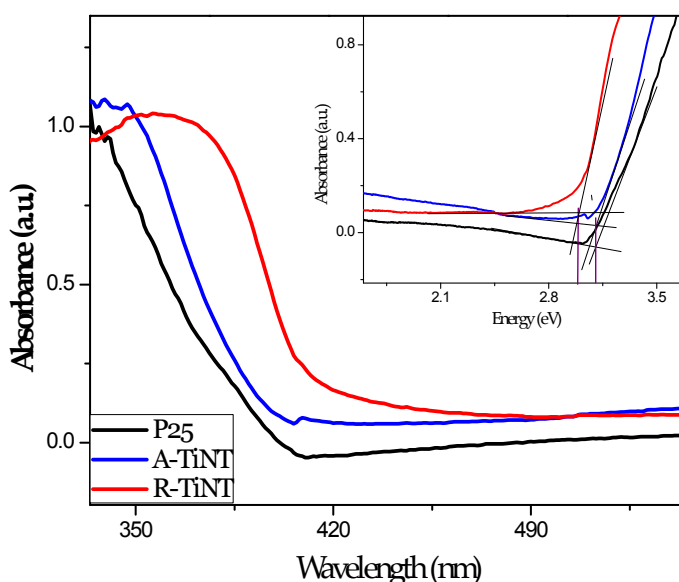


Figure S12: UV DRS absorbance spectrum different TiO_2 samples, Inset showing corresponding energy plot.

Photocatalytic degradation:

Rhodamine-B dye is a poly aromatic hydrocarbon of xanthene class. Photocatalytic removal of the complex dye molecule by harnessing visible light was carried out in batch photoreactor. The reaction setup consist of a simple glass reactor fitted with magnetic stirrer for continuous stirring to ensure uniform catalyst distribution. The reactor was kept at a distance of 30 cm from the light source (80W LED lamp).

Photodegradation was carried out for 4 hours of total reaction, with 1 hour dark adsorption phase followed by 3 hours of illuminated photoreaction phase. Aliquots of samples (2 ml) taken at regular intervals (10 min interval for first hour of illumination, 20 min interval for next 2 h) were

collected. Centrifugation (SPINWIN-MC01) of samples (as soon as collected) at 10,000 rpm for 10 min to separate the catalyst particles from reaction solution was performed to cease further photoreaction.

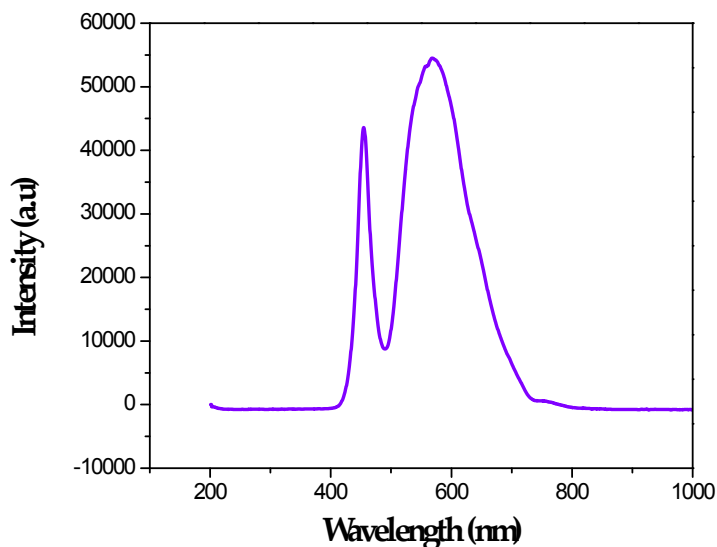


Figure S13: LED lamp spectrum.

Quantification method:

UV-Vis spectrophotometer (Shimadzu UV1800 series) was employed to analyze the degradation of Rhodamine-B samples. Concentration was calculated from the calibration curve plotted by analyzing known concentration (corresponding stock solution prepared before degradation experiment) of stock solution. The absorbance spectrum of the stock solution (20.8 μM) revealed the λ_{max} value (maximum absorbance) at 551 nm. Consistent λ_{max} value of 551 nm was obtained for all the calibration sample (20.8 μM to 1 μM) revealing linearity of calibration plot in this working concentration range. This is further confirmed from the correlation coefficient (R^2) of > 0.99 .

The change in concentration with respect to time was calculated from the corresponding calibration plot. Decrease in concentration was normalized to give percentage (%) degradation (equation 4) and degradation profile was given by plotting % degradation Vs. reaction time.

$$\% \text{ Degradation} = \left(1 - \frac{C_a}{C_0} \right) * 100 \quad (4)$$