

Electronic Supplementary Information

Deformation assisted fabrication of uniform spindle, tube and rod shaped nanoscale 3D TiO₂ architectures and their photocatalytic activity

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Experimental Details

Materials

Titanium tetraisopropoxide ($C_{12}H_{28}O_4Ti$, TTIP), Hydrochloric acid (HCl, 20%), Cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, CTAB), Stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$), Sodium hydroxide (NaOH) and ethylene glycol (EG) were purchased from Dae-Jung chemicals, Korea. For photocatalysis experiments, Potassium Dichromate ($K_2Cr_2O_7$) was purchased from Junsei Chemicals, Korea. All precursors were used as received, without purifying further. Deionized water was used throughout the experiments.

Preparation of Thorn-ball shaped TiO_2 nanostructures

Step 1: Preparation of precipitates

An aqueous solution (refer Scheme 1, Solution A) was prepared by dissolving 5 mM of CTAB and 10 mM of $SnCl_2 \cdot 2H_2O$ in 25 ml of DI water. Appropriate quantity (1 - 2 ml) of TTIP was dissolved in 15 ml of HCl (refer Scheme 1, Solution B). Solutions A and B were mixed together under vigorous magnetic stirring to yield the precipitates (Solution C). Solution C was allowed to settle down naturally and then by centrifugation, the white precipitates were collected. The pure precipitate was dried in an oven at 100 °C for 10 h.

Step 2: Preparation of Thorn-ball nanostructures (TBN)

20 ml of solution-C (from, Step 1) was mixed with 30 ml of EG and this final solution was transferred to a 100 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and the hydrothermal reaction was carried out at 150 °C for 18 h. After the reaction was over, the autoclave was allowed to cool down naturally. The dark slurry containing white colored sediments was transferred to a clean beaker with the addition of excess ethanol. After the white sediments settled at the bottom, the dark colored solution was discarded. The white sediments were centrifuged several times with ethanol to

remove impurities such as CTAB, HCl and EG. Pure sample obtained after centrifugation was dried in an oven at 100 °C for 10 h.

Preparation of STN

STN is fabricated by sintering TBN at 500°C, respectively for 1 h. For a comparison and to elucidate the formation mechanism of STN, the precipitate sample was also sintered at 500 °C (Fig. S3).

Preparation of Tube like 3D TiO₂ nanostructures (TNT)

15 mg of TBN was dissolved in 60 ml of 10M NaOH solution and this solution was transferred to an autoclave of 100 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and the hydrothermal reaction was carried out at 110 °C for 20h. The sediments were separated by centrifugation with excess DI water and the operation was repeated until the pH of the solution was 7. The final centrifuged sediment was dried in an oven at 100 °C for 10 h.

Preparation of rod like 3D TiO₂ nanostructures (TNR)

TNR is fabricated by sintering TNT at 500 °C for 1 h.

Characterization Details

X-ray diffraction (XRD) patterns of the prepared samples were obtained using an X-ray diffractometer (*Rigaku-Dmax 2500*) with Cu-K α radiation ($\lambda = 0.15405$ nm, 40 kV, 100 mA). Samples were scanned in the range $2\theta = 20 - 80^\circ$. Morphology and Energy dispersive X-ray spectroscopy studies (EDS) were performed using *MIRA3 TESCAN* high resolution scanning electron microscope (SEM) equipped with a high brightness Schottky field emission gun. UV-Vis Diffuse reflectance spectrum (DRS) of the photocatalysts were recorded using *JASCO V-550* UV-Visible spectrophotometer equipped with an integrating sphere (*JASCO ISV-469*) using a dedicated powder sample holder (*JASCO PSH-001*). Surface area of the samples were estimated by measuring the nitrogen adsorption-desorption isotherms on a *Micrometrics ASAP 2020* system. All the samples measured were degassed at 300 °C for 3 h prior to the actual measurements. High-resolution transmission electron microscopy (HRTEM), EDS and selected

area electron diffraction pattern (SAED) were performed using *JEOL 2010F* FE-TEM operating at 200 kV. The samples for TEM were prepared by dropping a few drops of the sample solution dissolved in ethanol on a lacey carbon TEM grid.

Experimental details for the photocatalytic reduction of Cr(VI)

Cr(VI) degradation experiments using the fabricated nanostructures were conducted under both UV and visible light irradiations. The concentration of the reaction slurry was 50 ppm ($K_2Cr_2O_7$ in DI water) and the catalyst concentration was 1 g/L. 200 ml of the reaction slurry was prepared in a beaker and appropriate amount of HCl was added, such that the pH was 3. Slurry was then stirred under dark for 1 h to ensure the adsorption of Cr(VI) ions on the surface of the photocatalyst. Experiments under UV light source were conducted under a UV lamp with the power of 300 W (Raynics, Korea). Visible light photocatalysis experiments were conducted in a home-made irradiation system was constructed using a 100 W Halogen lamp (HI-Spot 95) purchased from Osram Sylvania Inc, with UV-stop feature. A water bath was used to cool down the reaction slurry. The slurry on the water bath was placed on top of a magnetic stirrer, 7 cm below the source and was agitated at 200 rpm. Aliquots were collected at regular intervals of time in both the cases. UV-Vis absorption spectra of the aliquots were recorded on a JASCO V-550, UV-Visible spectrophotometer.

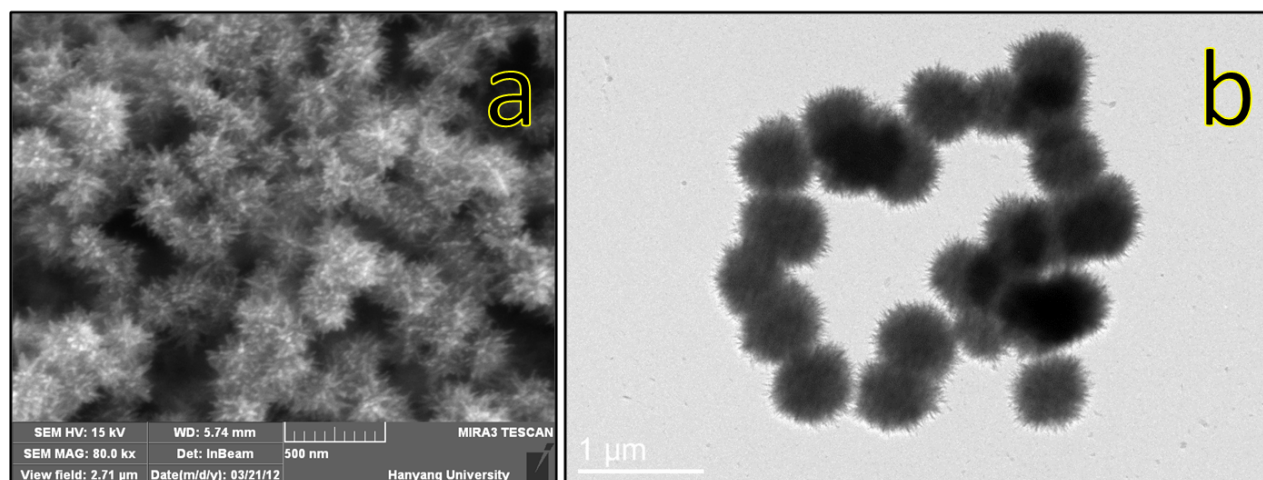


Fig. S1 (a) SEM and (b) TEM images of TBN nanostructures.

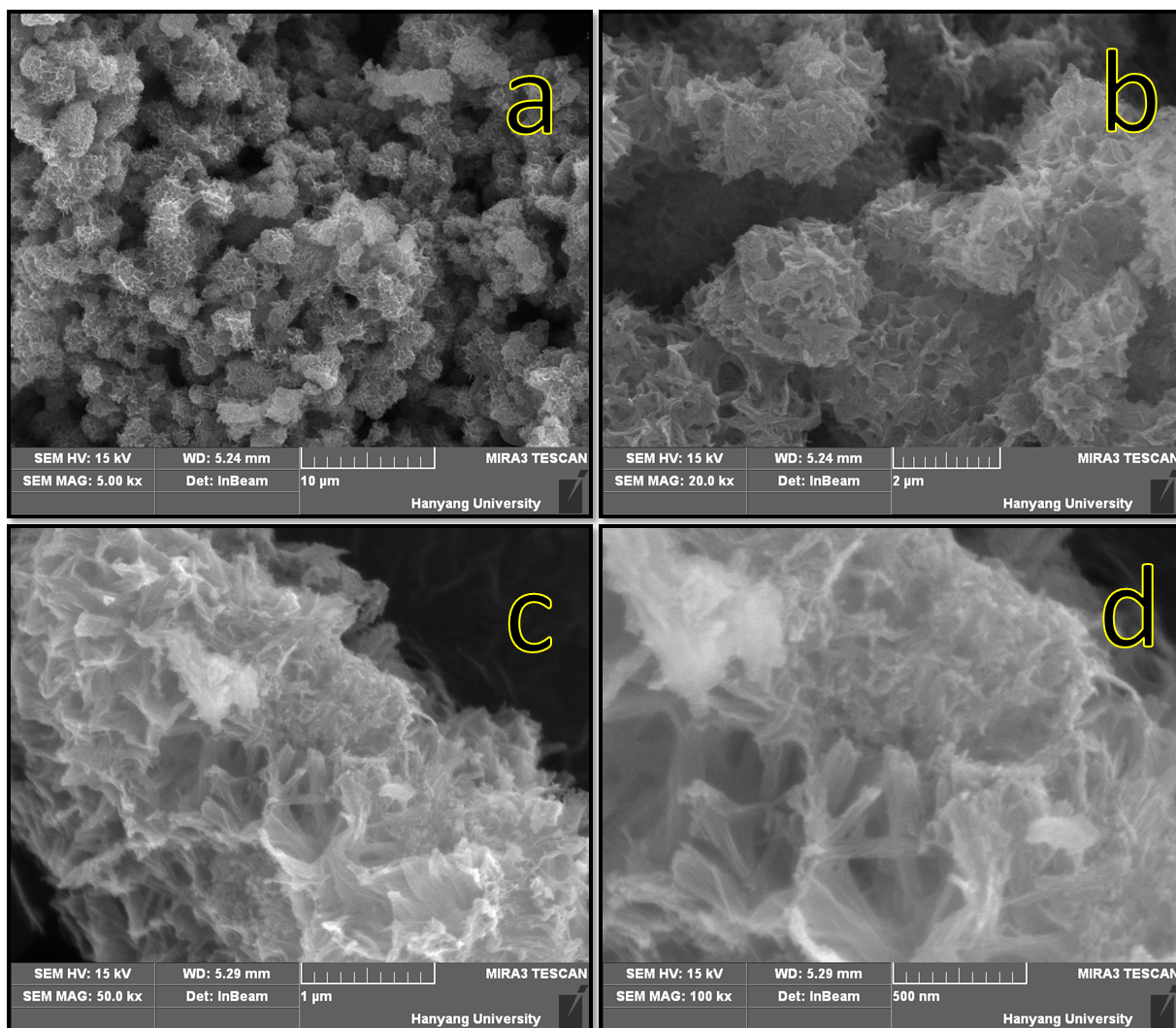


Fig. S2 SEM images of Tube like TiO₂ nanostructures (TNT) under different magnifications depicting a 3D morphology.

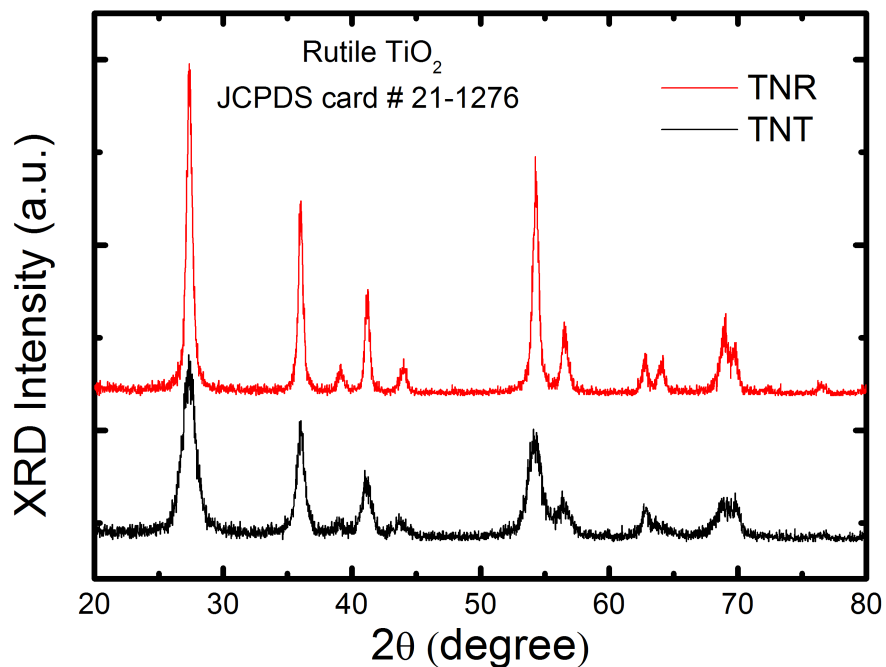


Fig. S3 XRD patterns of TNT and TNR depicting the rutile phase of TiO₂.

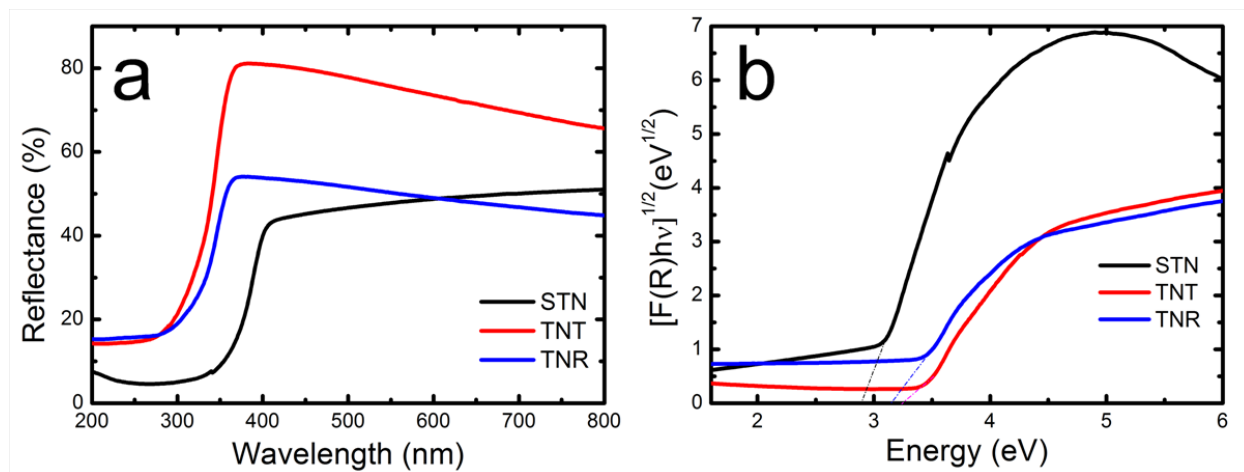


Fig S4. (a) Diffused reflectance spectra (DRS) of the fabricated nanostructures and (b) their corresponding Tauc plots.

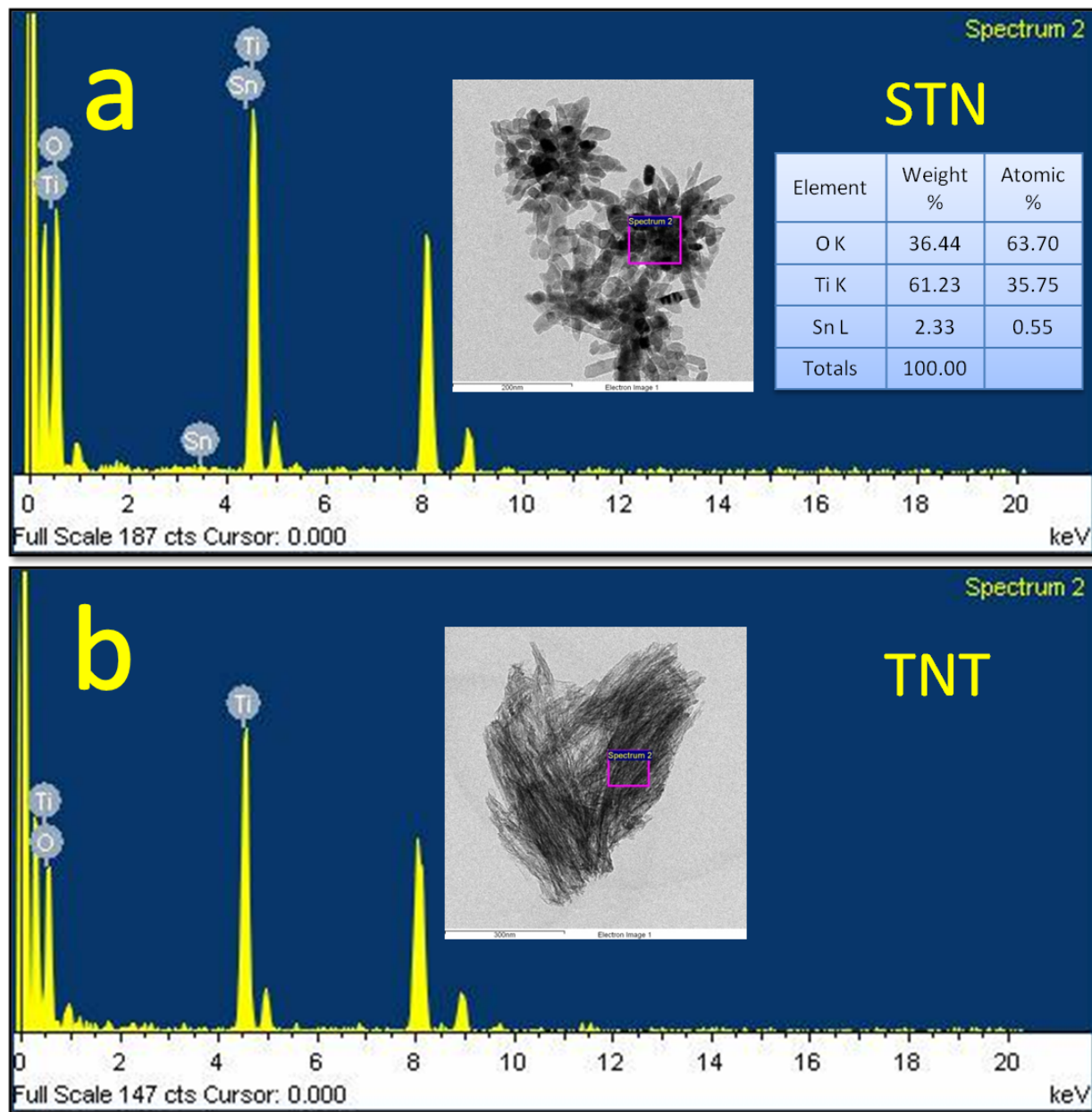


Fig. S5 Energy dispersive X-ray spectra (EDS) of (a) STN and (b) TNT, obtained from the area marked in the micrographs shown in the insets. TNT is fabricated by the chemical deformation of TBN and during this process Sn^{2+} atoms are etched by NaOH. The absence of Sn peaks in the EDS spectra of TNT can be attributed as the reason for the increase in its energy bandgap (E_g).

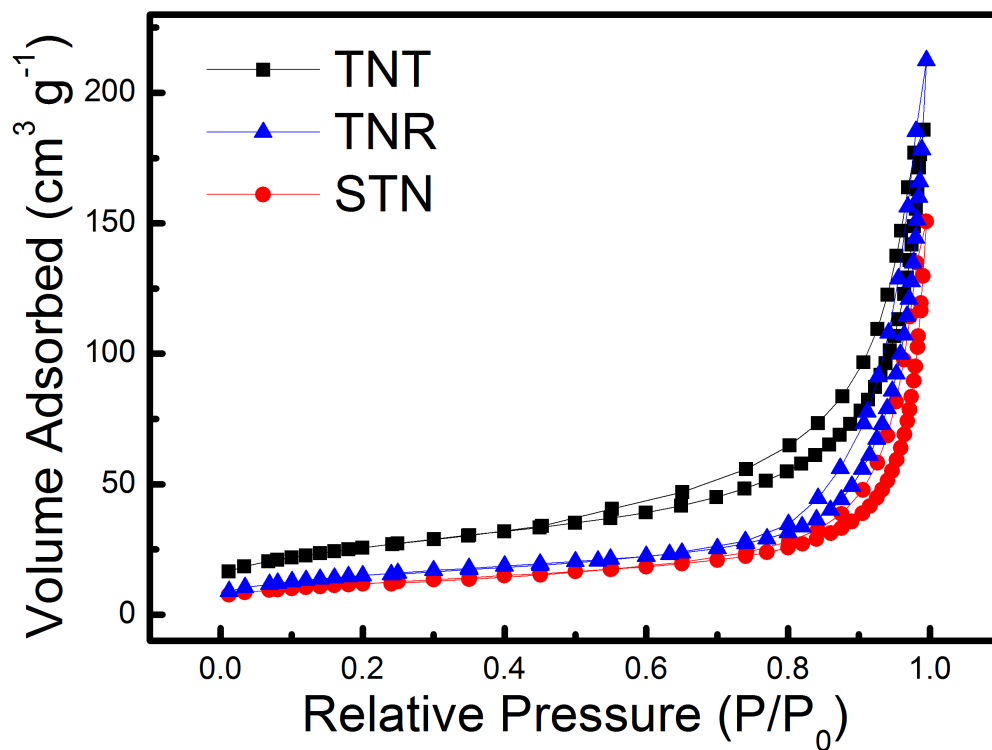


Fig. S6 Nitrogen adsorption-desorption isotherms of the fabricated samples obtained at 77 K.

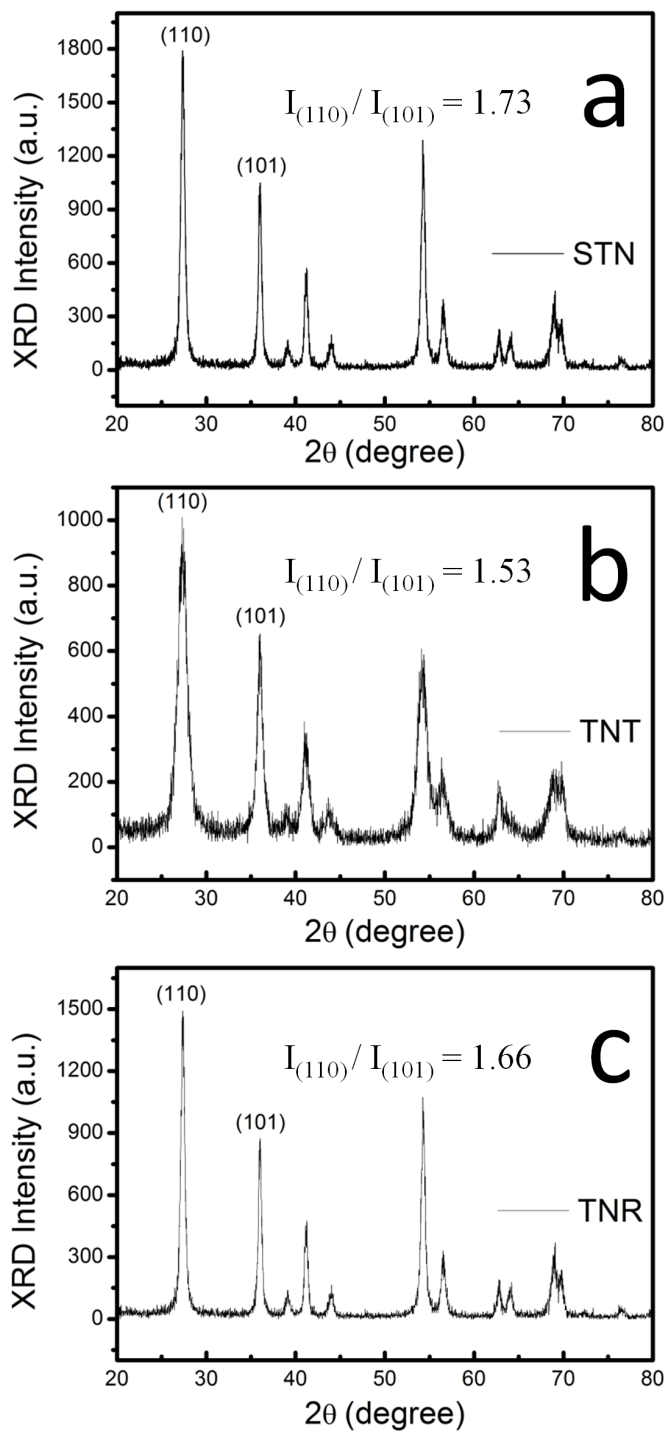


Fig. S7 XRD patterns of the 3D TiO₂ nanostructures prepared by the deformation of TBN. (a) STN, (b) TNT and (c) TNR. The intensity ratio between the (110) and (101) diffraction peaks are mentioned for each system. The results indicate that STN contains the highest intensity of photoactive (110) facets.