

Supporting Information for “Polymorphism- induced catalysis difference of TiO₂ nanofibers for rechargeable Li-O₂ batteries”

*Seung Ho Kang,[‡] Kyeongse Song,[‡] Jaepyeong Jung, Mi Ru Jo, and Yong-Mook Kang**

Department of Energy and Materials Engineering, Dongguk University-Seoul, Seoul 100-715, Republic of Korea

[‡] These authors contributed equally.

* Corresponding author E-mail: Yong-Mook Kang; dake1234@dongguk.edu

Experiment details

Preparation of TiO₂ NFs by electrospinning: Titanium(IV) isopropoxide (Ti[OCH(CH₃)₂]₄, 99%), acetic acid (CH₃COOH, 99%), and poly-(vinylpyrrolidone) (PVP, M_w = 1,300,000) were purchased from Aldrich. First, to prepare the electrospinning solution, 1.6 mL of titanium(IV) isopropoxide was mixed with 5.9 mL ethanol and 0.5 mL of acetic acid. Following this, the solution was added to 5 mL of an ethanol solution containing 0.585 g of PVP. The solution then underwent stirring for 1 h. The mixture was immediately loaded into a plastic syringe equipped with a 23 gauge SUS needle. The needle was connected to a high-voltage supply that was generating a DC voltage of 14 kV. The feeding rate for the precursor solution was 0.5 mLh⁻¹ using a syringe pump and the needle-to-collector distance was 9 cm. The electrospinning process was conducted in air. After the electrospinning, the electrospun NFs were left in air for 1 day for hydrolysis. To prepare the anatase TiO₂ NFs, the expoliated electrospun NFs were loaded on alumina boats, and heated at 450 °C for 1 h under air. For the rutile TiO₂ NFs, electrospun NFs heated at 750 °C for 5 h under air.

Electrochemical Measurement: The electrodes in this study were fabricated by a mixing TiO₂ catalyst nanoparticles, Ketjen black (EC600JD), and PVDF-HFP copolymer with a weight ratio of 40:45:15 by using N-methylpyrrolidone (NMP) as a solvent. The resulting slurries were pasted onto the carbon paper (GDL; Gas diffusion layer) and then dried in a vacuum oven at 120 °C for 5 h. After drying, the electrochemical properties of the prepared electrodes were evaluated by using Swagelok-type cells assembled in an argon-filled glove box. Lithium metal foils were used as a counter electrode, glass fiber disk as the separator and 1M LiCF₃SO₃ solution in tetraethyleneglycol dimethylether (TEGDME) as the electrolyte. Subsequently, the sealed cell was removed from the argon-filled glove box and then purged with O₂ gas (99.995%) for 10 min at 1 sccm, galvanostatically charged and

discharged at a current density of $200 \text{ mA} \cdot \text{g}_{\text{carbon}}^{-1}$ over a range of 2.0 - 4.5 V. For the stabilization of cycling, the cell was also tested using a constant current – constant voltage (CC – CV) mode with potentiostatic steps at 4.2 V under limited capacity condition ($1000 \text{ mAh} \cdot \text{g}_{\text{carbon}}^{-1}$).

Structural Characterization: TiO_2 NFs were characterized by an XRD (Bruker/New D8 Advance) diffractometer using graphite-mono-chromatized $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA, and a field emission scanning electron microscope (FE-SEM; JEOL JSM-6700F, operated at 10 and 30 kV). Bright-field TEM imaging and fast fourier transform diffraction pattern were conducted using a Tecnai G2 F30 operated at 300 kV accelerating voltage. Chemical compositions were analyzed using X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific Co. theta probe base system). All binding energies were referenced to the C 1s peak (284.5 eV). Finally, the pore volume and surface area of anatase and rutile TiO_2 NFs were estimated by Barret–Joiner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) analyses, respectively.

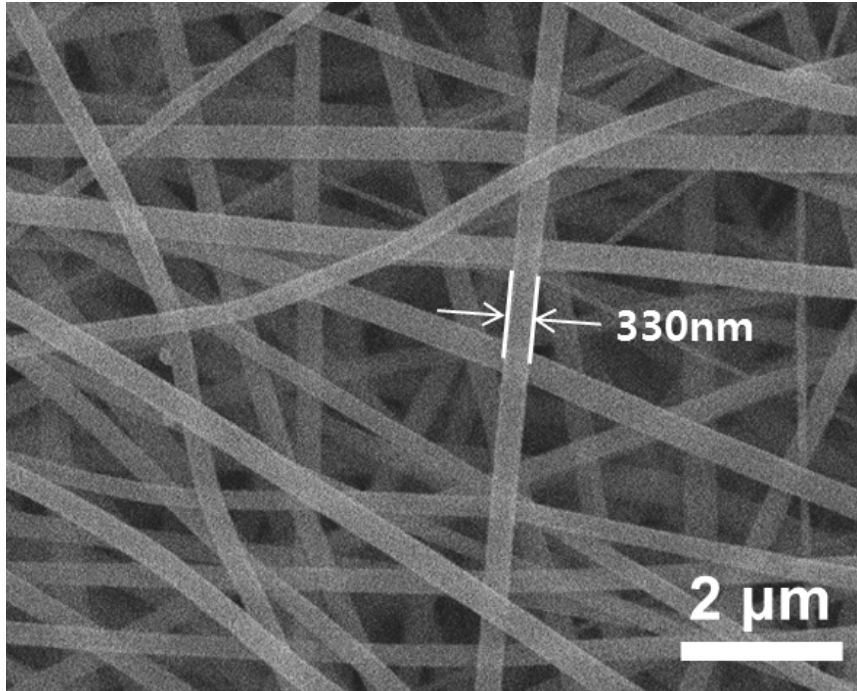


Figure S1. SEM image of electrospun NFs, which are composed of Ti precursor and PVP as supporting polymer.

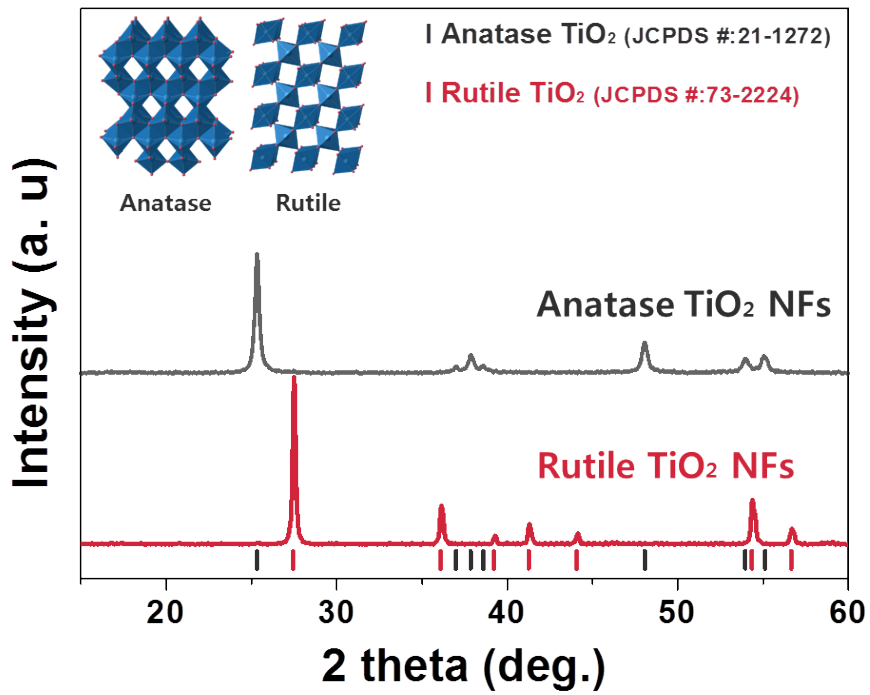


Figure S2. XRD patterns of the anatase (black line) and rutile (red line) TiO₂ nanofibers.

Inset: Schematic of the crystal structure, respectively.

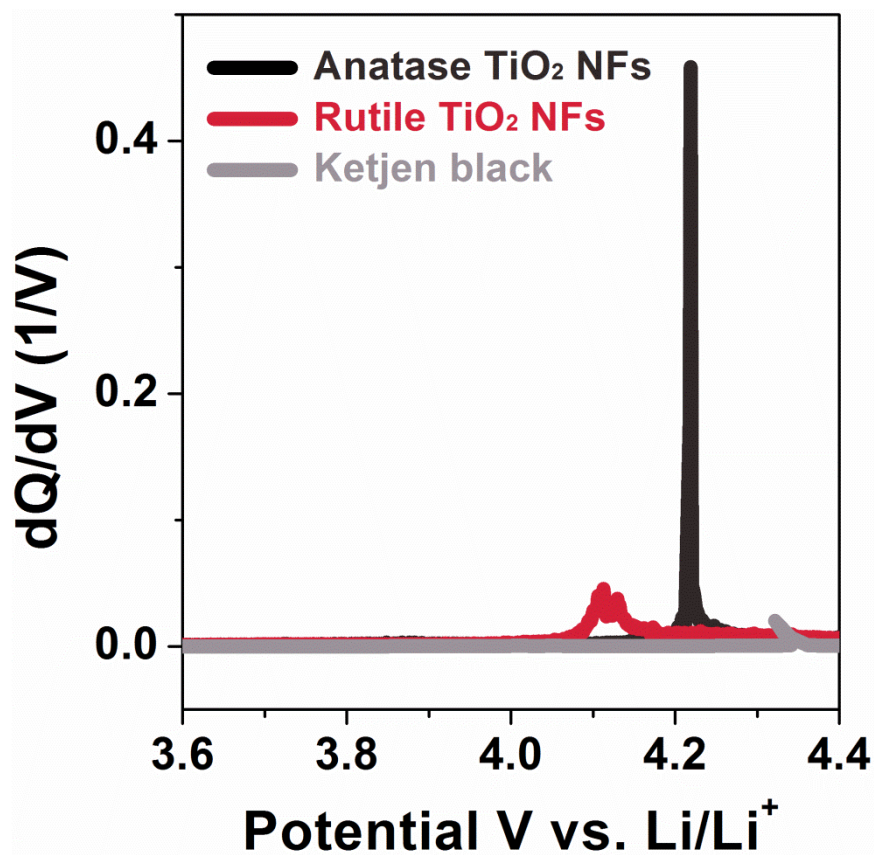


Figure S3. The differential charge capacity profiles of TiO₂ NFs.

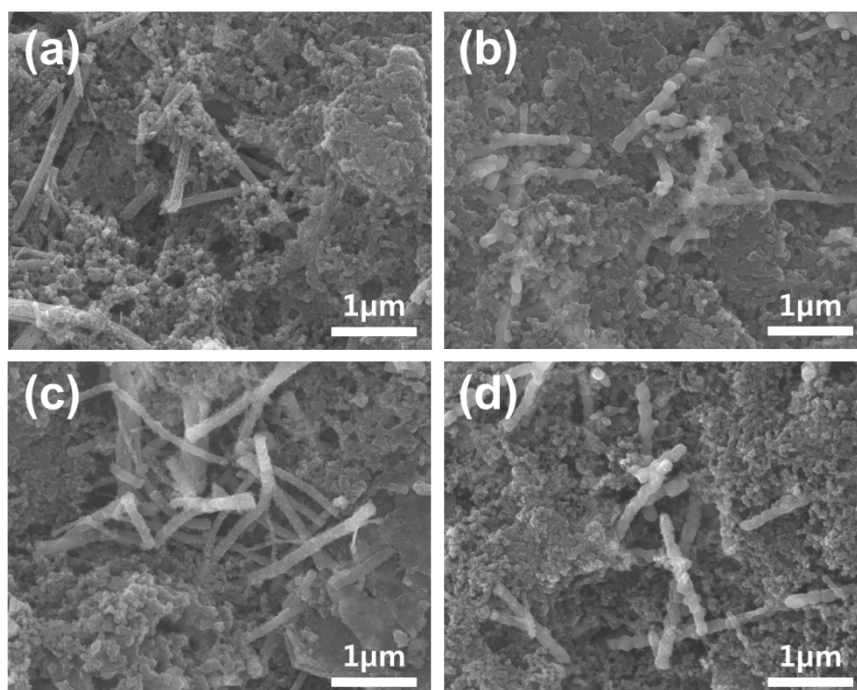


Figure S4. SEM image of (a) the pristine anatase TiO₂ NFs electrode, (b) the pristine rutile TiO₂ NFs electrode, (c) anatase TiO₂ NFs electrode after 1st charge, (d) rutile TiO₂ NFs electrode after 1st charge.

Table S1. The BET surface area and pore volume for TiO₂ NFs.

Properties	Anatase TiO₂ NFs	Rutile TiO₂ NFs
S_{BET} (m²·g⁻¹)	46.188	9.642
V_P (cm³·g⁻¹)	0.1483	0.0928

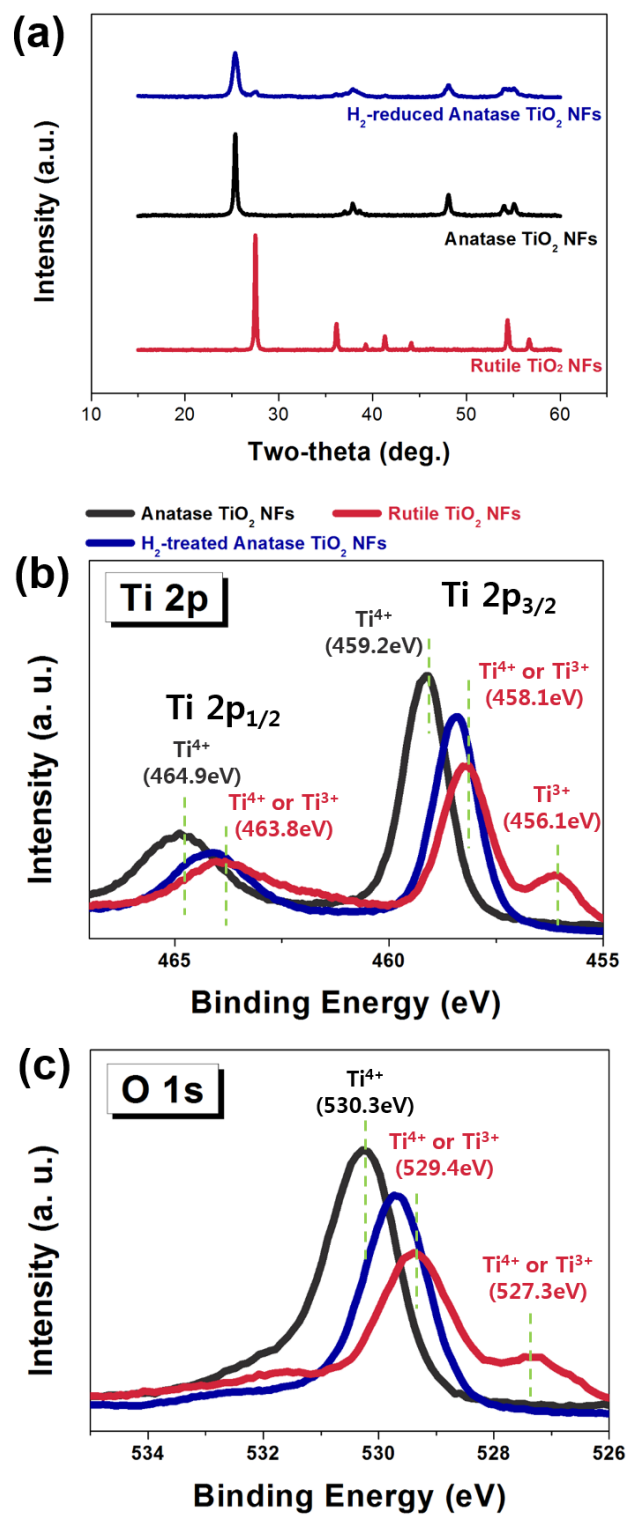


Figure S5. (a) XRD patterns of H_2 -reduced anatase, pristine anatase and rutile TiO_2 nanofibers. XPS spectra of H_2 -reduced anatase, pristine anatase and rutile TiO_2 NFs; (b) Ti 2p partial spectra (c) O 1s partial spectra.

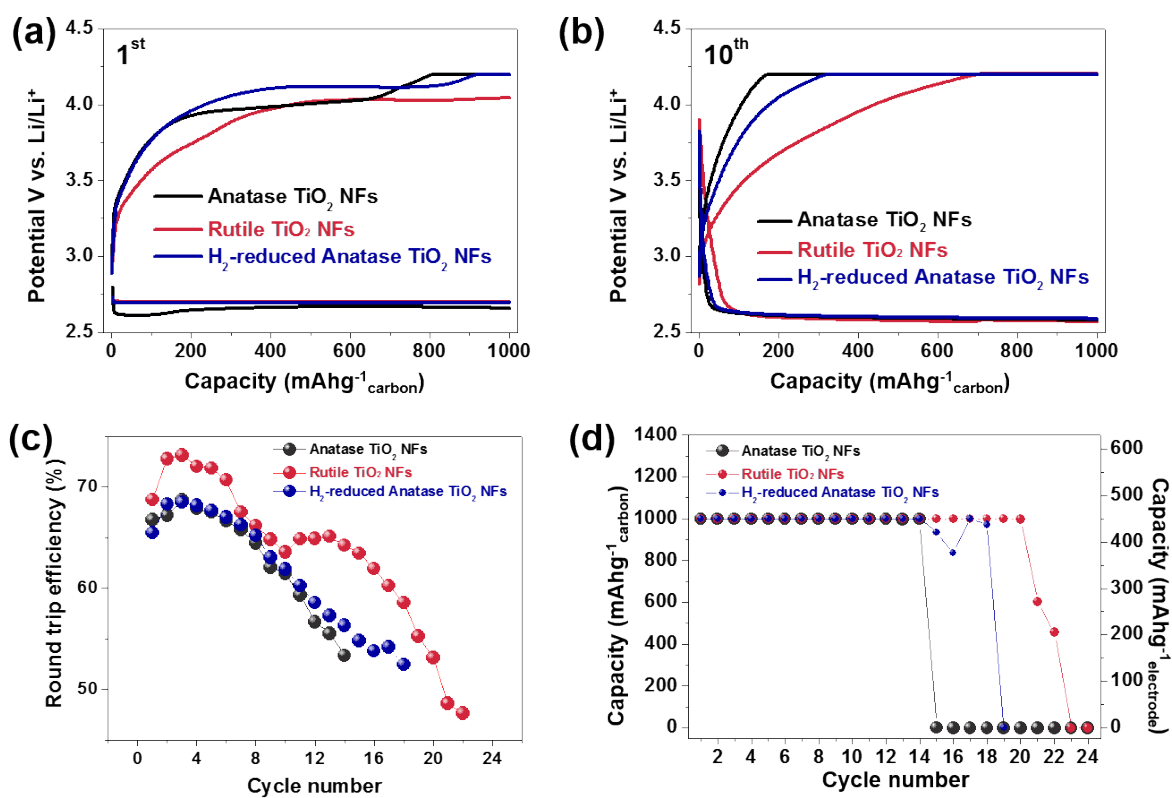


Figure S6. The electrochemical performances of Li-O₂ cells adopting TiO₂ NFs as cathode catalysts and their comparison with H₂-reduced anatase TiO₂ NFs; (a) The initial and (b) 10th discharge/charge profiles, (c) The Round-trip efficiency, (d) The cycle life when the capacity is limited below 1000 mAh·g⁻¹_{carbon}.

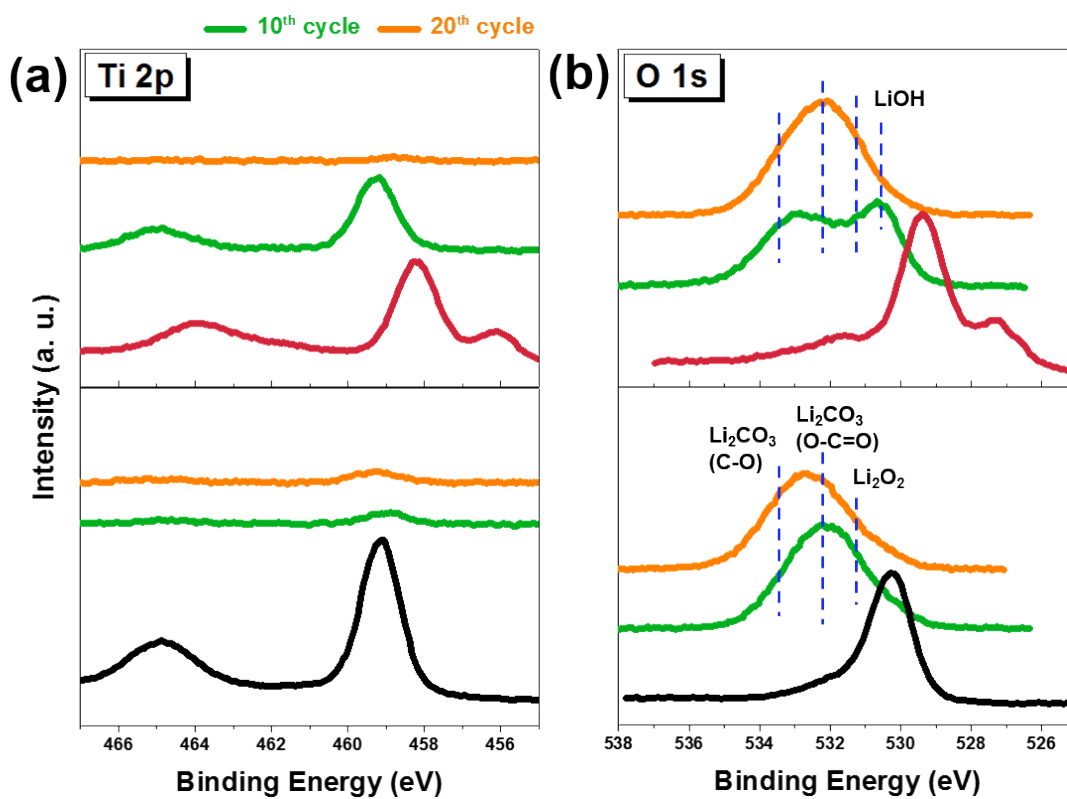


Figure S7. XPS spectra of rutile TiO₂ NFs (red) and anatase TiO₂ NFs (black) after 10th and 20th cycles; (a) Ti 2p partial spectra (b) O 1s partial spectra.

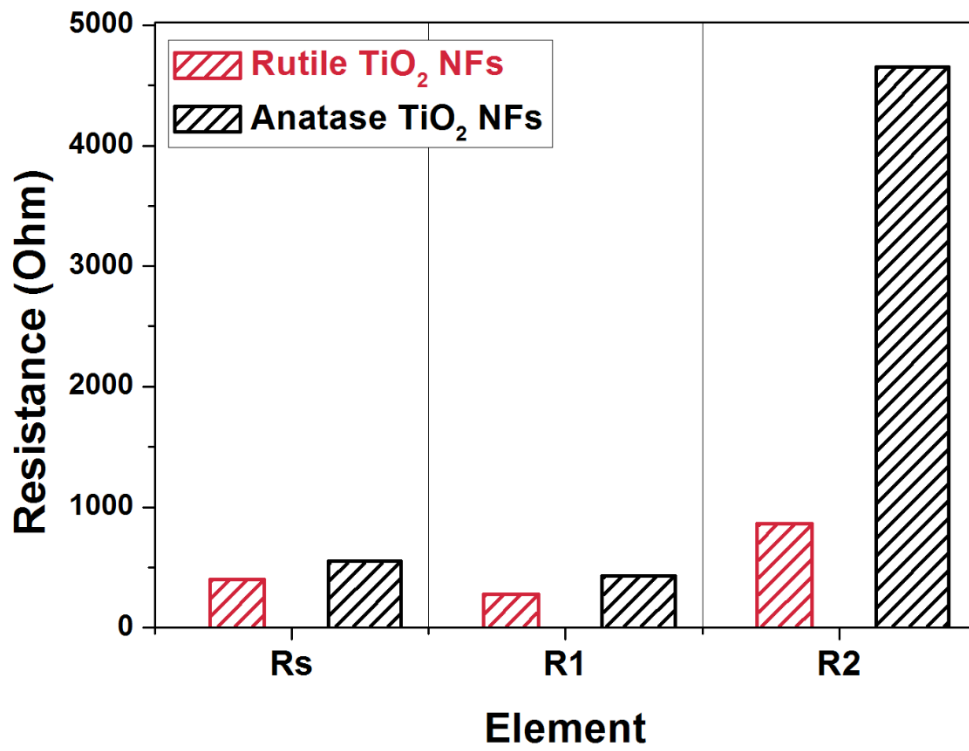


Figure S8. Equivalent circuit parameters (R_s , R_1 and R_2) of rutile and anatase TiO₂ NFs