

Electronic Supplementary Information

Calixarene functionalization of TiO₂ nanoarrays: an effective strategy for enhancing the sensor versatility

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Experimental section

Materials

Solvents Acetone (Scharlau, analytical grad) and toluene (Loba Chemie, 99.0%) were dried according to standard procedures, stored over activated 4 Å molecular sieves and degassed prior to use. Hydrochloric acid 37.0% and isopropoxide 97.0% were purchased from Sigma Aldrich and were used without purification. However, acetonitrile of spectroscopic grade from Aldrich was used in the spectroscopic measurements.

FTO substrates (Tec, 10 Ω, 137 nm) were purchased from Visiontek Systems Ltd. Prior to use, all FTO substrates were ultrasonically cleaned during 15 min with consecutively acetone and iso-propanol, and rinsed with deionized water, then finally dried in air at room temperature. TiO₂NRs and TiO₂NTs materials were prepared following reported procedures.^{1,2}

Synthesis of 1-3@TiO₂NRs and 1@TiO₂NTs

For the grafting of TiO₂NRs and TiO₂NTs, **1** (25.0 mg / 3.85 μmol), **2** (34 mg / 8.04 μmol), and **3** (69 mg / 7.97 μmol) was dissolved in 25 mL of toluene and was stirred over a plate of TiO₂NRs for 48 h at reflux and under nitrogen atmosphere. The experiments were carried out in darkness. After cooling to room temperature, the as prepared **1-3**@TiO₂NRs and **1**@TiO₂NTs were removed, rinsed with hot toluene, and dried with N₂.

Characterisations of 1-3@TiO₂NRs and 1@TiO₂NTs

X-ray diffraction (XRD) spectra were obtained with a Bruker AXS D8 Advance instrument with CuK_{α1} radiations (λ = 1.5406 Å) and 1D LynxEye detector (Silicon Drift Detector) for 2θ ranging from 20° to 70°. The samples were deposited on quartz and the measurements were performed at a grazing-incidence angle, larger than the so-called critical angle for total external reflection, at which X-ray penetrates the sample.

Micro Raman spectra were recorded at room temperature with a WITec alpha300 R confocal Raman microscope, coupled to a frequency doubled Nd:YAG laser (532 nm) and a 300 mm focal length lens-based spectrometer (WITec broadband UHTS 300 VIS-NIR), equipped with a 600 lines/mm grating and a thermoelectrically cooled (213 K) front-illuminated CCD detector with 1650×200 pixel. The sample is manually positioned along x, y, z directions and is lightened with LED white-light for Köhler illumination. All the spectra were recorded using a Zeiss EPIPLAN 100×/0.8 objective. An integration time of 3 s and 30 accumulations were used in all

experiments. For each sample, Raman spectra were recorded at different areas to ensure reproducibility.

Infrared spectra (400 – 4500 cm^{-1}) were recorded using a Bruker VERTEX 80v instrument after 64 scans. The samples are thin films of TiO_2NRs and TiO_2NTs , and KBr pellets of calixarenes. Diffuse reflectance mode based on the Kubelka-Munk function (correlation between the reflectance and the concentrations of absorbing species in weak absorbing samples) was used

$$\text{for } \text{TiO}_2\text{NRs/NTs. } F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} = \frac{A \times C}{s}$$

(R =reflectance; k =absorption coefficient; s =scattering coefficient; c =concentration of the absorbing species; A =absorbance).

Absorption mode was applied for calixarene. All measurement were performed in vacuum and under nitrogen atmosphere. Measurements were collected before and after grafting in order to evidence the attachment of calixarenes.

Solid-state reflectance absorption spectra were recorded at room temperature by diffuse reflectance using a Cary 5000 UV-Vis-NIR spectrophotometer equipped with an integrating sphere. Before spectra were recorded, a baseline, with barium sulfate, was obtained. UV-Vis absorption spectra in acetonitrile were recorded on Shimadzu UV-2100 at 293 K. Cuvettes of 1.0 cm optical path length were used. Solid-state fluorescence spectra were recorded at variable temperatures 50-310 K with a Horiba FluoroMax-4 spectrometer controlled by FluorEssenceTM software and were corrected for the instrumental response.

Surface morphology was investigated with a TESCAN Vega3 SBH scanning electron microscope in Wild Field mode and with 5-20 kV voltage.

The wettability was measured using a Contact Angle System OCA 20 equipped with the software SCA 20. All samples were dried in a homemade oven at 50 °C and in vacuum for 5 hours. Then, two drops of 10 μL water were deposited on the top surface with an automated dosing system. When side view images of the drops were captured at a rate of 10 frames per second, contact angles were automatically calculated by fitting the captured drop shape to the one calculated by the tangent leaning method.³

Photoelectrochemical detection of profenofos

The photo-response of **1@TiO₂NRs** was evaluated by measuring the photocurrent density J_p , using a scanning potentiostat (Metrohm AUTOLAB PGSTAT12 Instrument). The measurement of the photocurrent density as a function of the applied potential E was performed in a standard three-electrode configuration (single-compartment) home-made cell.⁴ The potential of each prepared sample, as working electrode, was measured using an Ag/AgCl reference electrode and a Pt wire counter electrode. A solution of Na_2SO_4 (0.5 M, pH = 7) was used as electrolyte. The whole cell was purged with argon to remove any dissolved oxygen prior to experiment. A surface of 0.5 cm^2 was illuminated using a 150 W Xenon lamp (ORIEL instruments) to mime solar light.

Gas sensing measurements of the 1-3@TiO₂NRs sensors

The sensor chip was placed in a stainless steel high-pressure chamber.⁵ The impedance measurements were performed at 290 K with two contacts made with silver paint using masks resulting in contacts of approximately 0.5 x 3 mm^2 , separated by a distance of 8 mm. A Digimess RLC300 Impedance Meter was used at 10 kHz to record constantly the variation of

the resistance of the sensor with gas (H₂, N₂) pressure injected in the chamber. The chamber is connected to a Sieverts type volumetric system⁶ composed of four pneumatic valves enclosing a calibrated volume. The pressure is measured with a KISTLER 4045KA100 piezoresistive transducer (0–100 bar). For experiments of series of load at low pressure 1 bar and discharge of hydrogen, a precise Milipore (0–1 bar) capacitive transducer was used for pressure measurements. A NTC thermistor monitors the temperature close to the reference volume of the Sieverts system.

References

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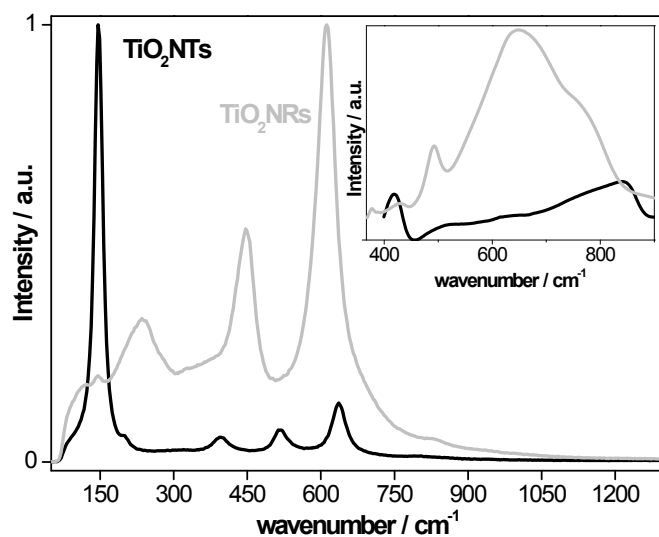


Fig. S1 Normalized Raman [Inset: IR] spectra of TiO₂NTs and TiO₂NRs.

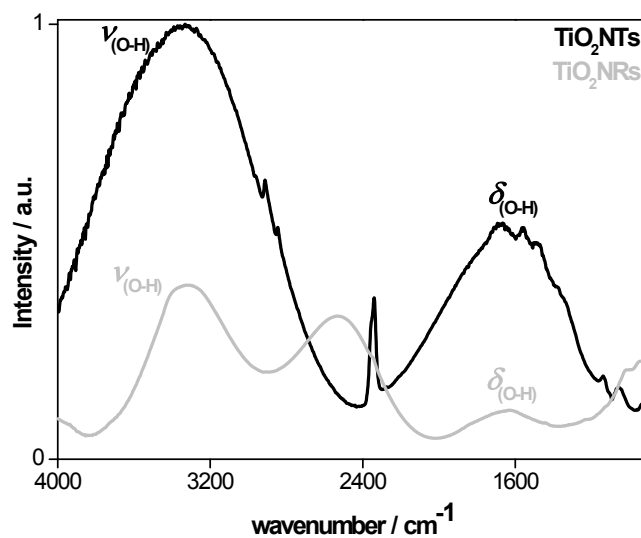


Fig. S2 Infrared spectra of rutile TiO₂NRs and anatase TiO₂NTs between 4000-900 cm⁻¹.

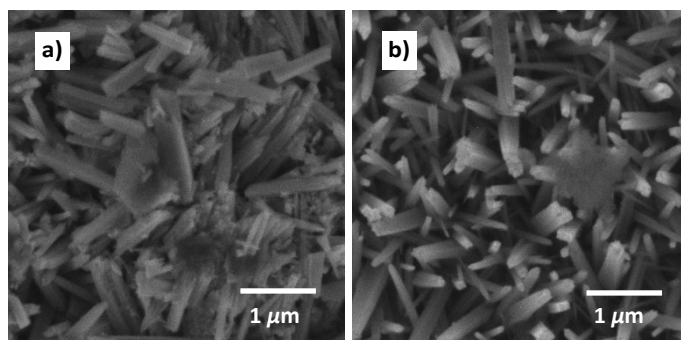


Fig. S3 SEM images of 2@TiO₂NRs (a) and 3@TiO₂NRs (b).

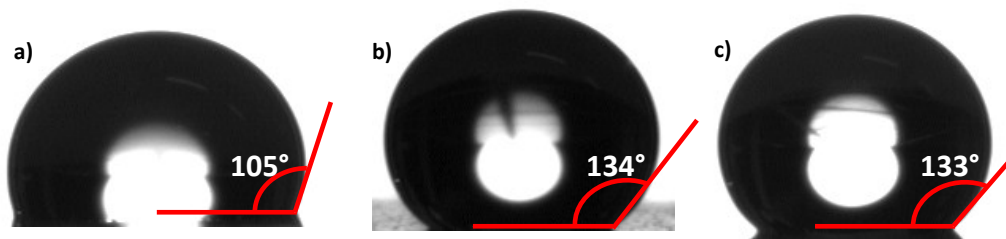


Fig. S4 Contact angle images of **1**@TiO₂NRs (a), **2**@TiO₂NRs (b), and **3**@TiO₂NRs (c).

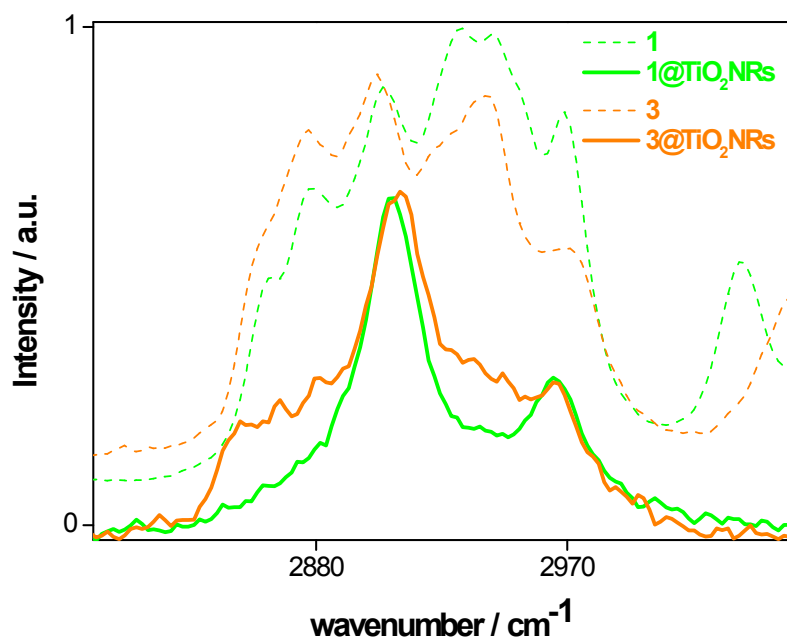


Fig. S5 Raman spectra of **1**, **1**@TiO₂NRs, **3**, and **3**@TiO₂NRs.

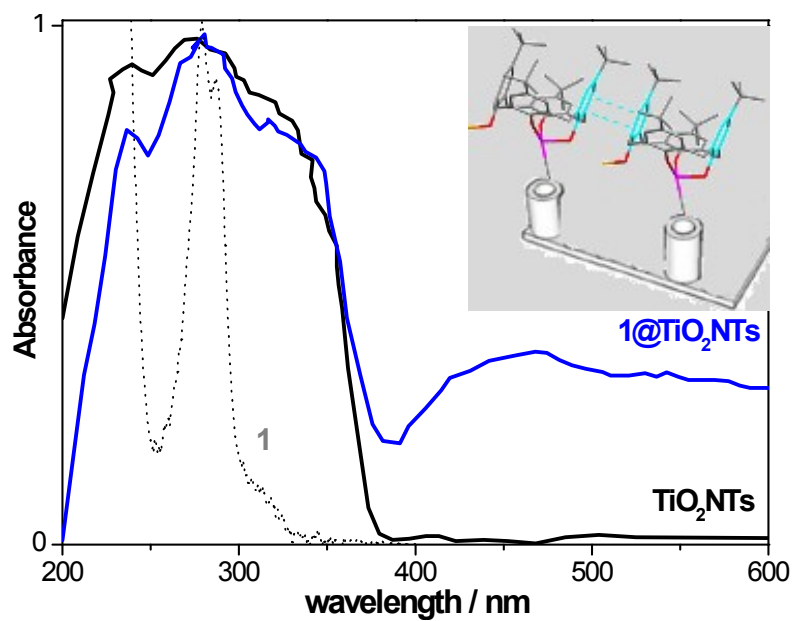


Fig. S6 UV-Visible spectra (b) of TiO₂NRs, TiO₂NTs, **1**, **1@TiO₂NRs**, and **1@TiO₂NTs**.

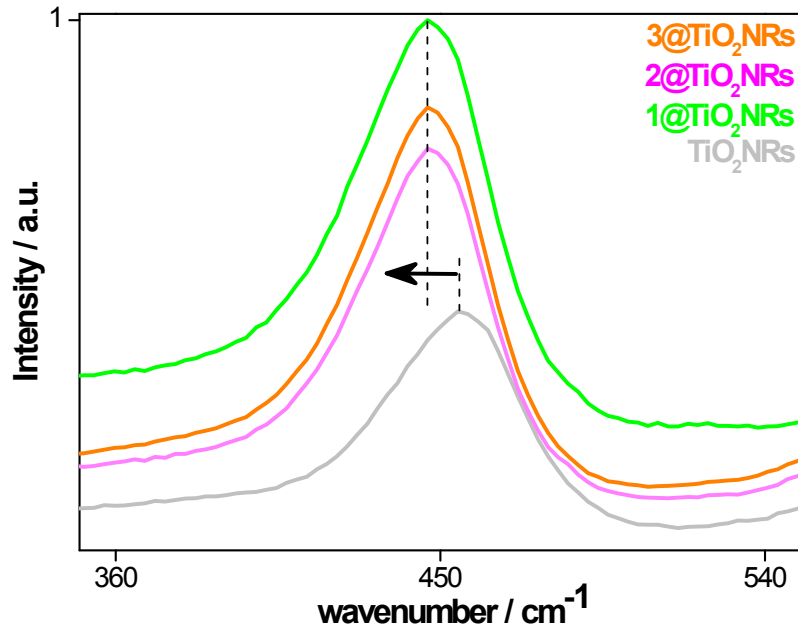


Fig. S7 Raman spectra of TiO₂NRs, **1@TiO₂NRs**, **2@TiO₂NRs**, and **3@TiO₂NRs**.

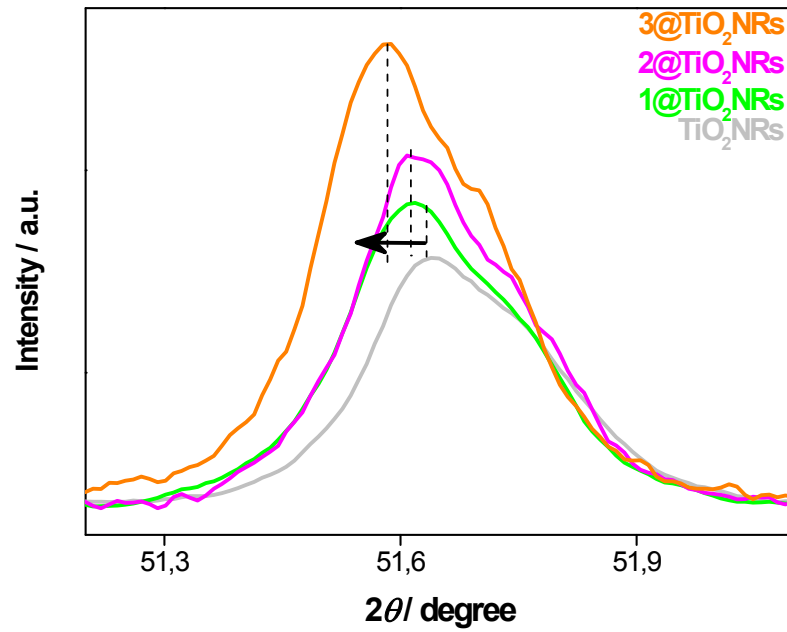


Fig. S8 XRD patterns of TiO₂NRs, **1@TiO₂NRs**, **2@TiO₂NRs**, and **3@TiO₂NRs**.

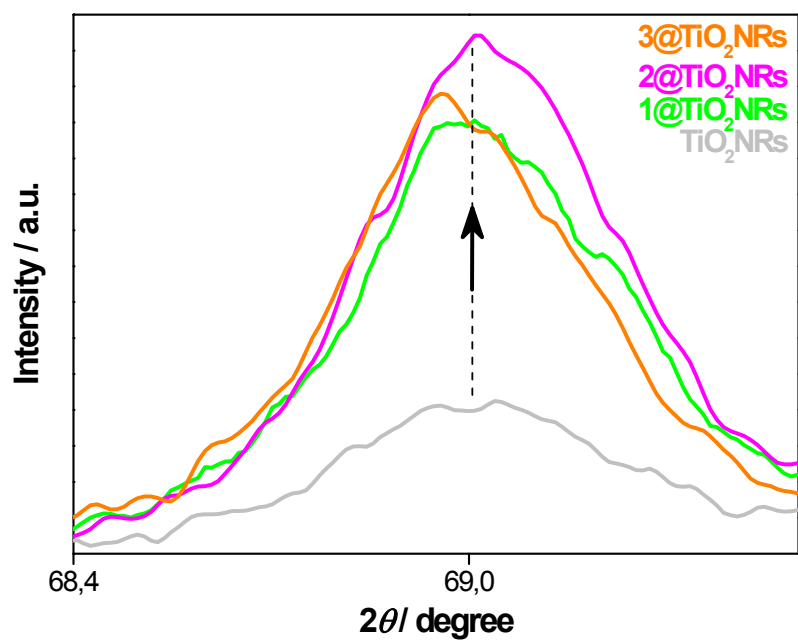


Fig. S9 XRD patterns of TiO_2NRs , $1@ \text{TiO}_2\text{NRs}$, $2@ \text{TiO}_2\text{NRs}$, and $3@ \text{TiO}_2\text{NRs}$.

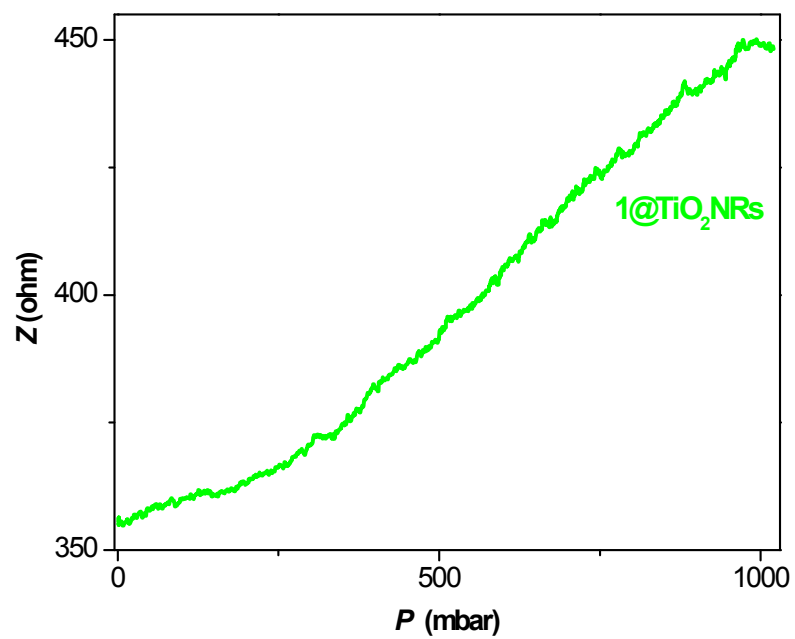


Fig. S10 Resistance variation in $1@ \text{TiO}_2\text{NRs}$ with nitrogen pressure at 290 K.

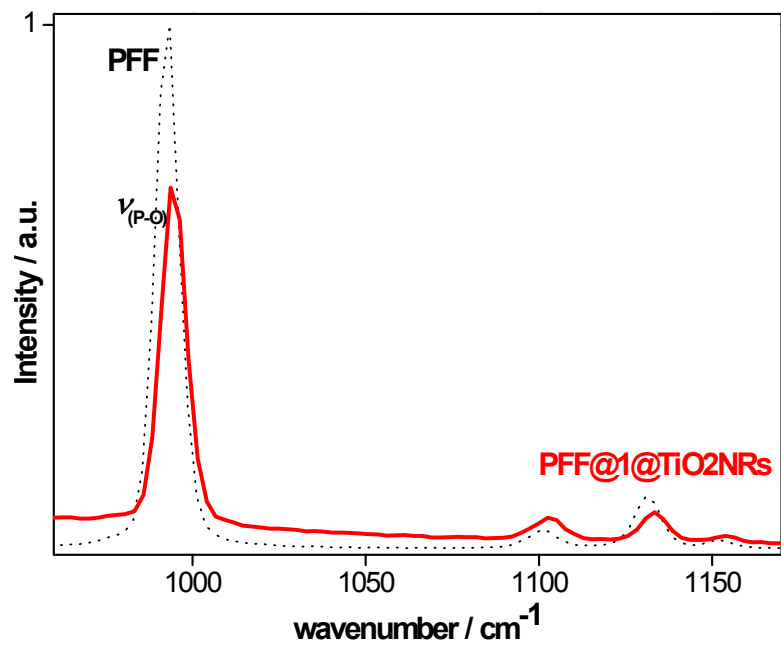


Fig. S11 Normalized Raman spectra of PFF and PFF@1@TiO₂NRs.

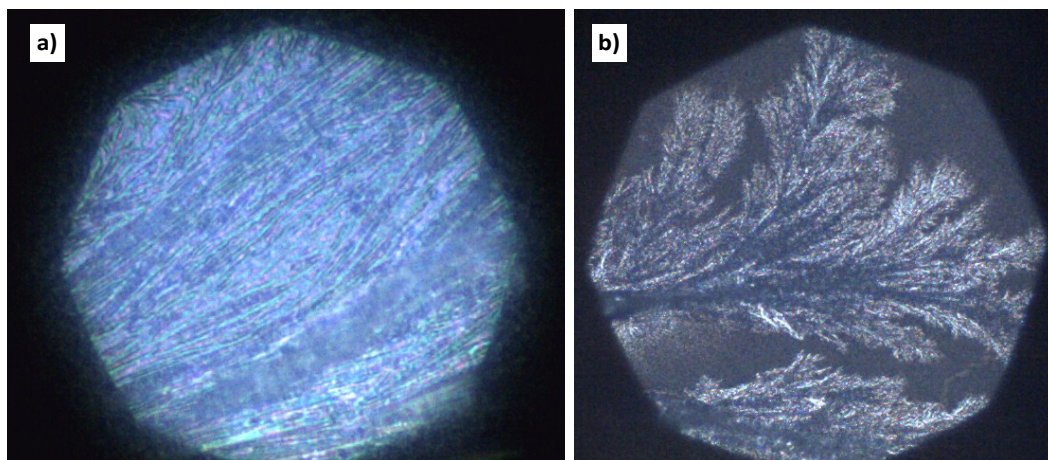


Fig. S12 Optical images of 1@TiO₂NRs (a) and PFF@1@TiO₂NRs.