

High Rate CO₂ Photoreduction Using Flame Annealed TiO₂ Nanotubes

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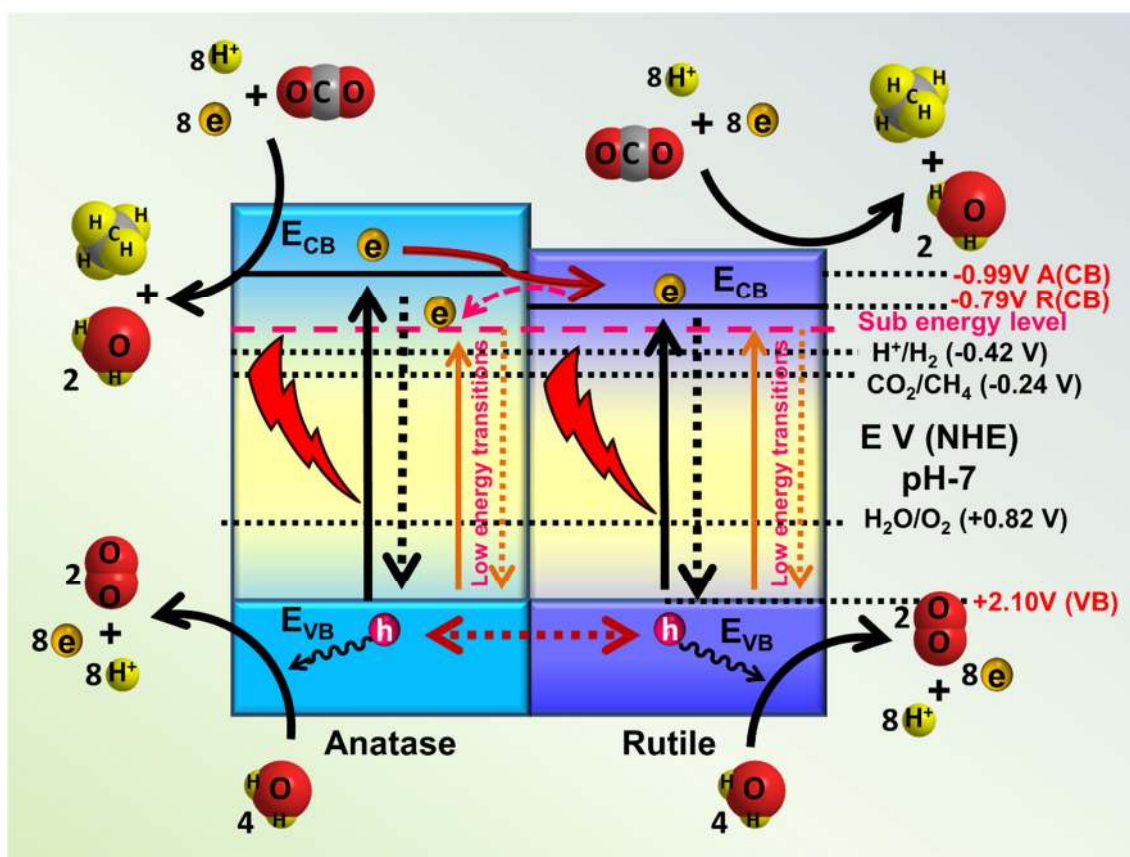
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TOC Graphic



Abstract

The photocatalytic reduction of CO₂ into light hydrocarbons using sunlight and water is a challenging reaction involving eight electron transfer steps; nevertheless, it has great potential to address the problem of rising anthropogenic carbon emissions and enable the use of fossil fuels in a sustainable way. Several decades after its first use, TiO₂ remains one of the best performing and most durable photocatalysts for CO₂ reduction albeit with a poor visible light absorption capacity. We have used flame annealing to improve the response of TiO₂ to visible photons and engineered a nanotubular morphology with square-shaped cross-sections in flame-annealed nanotubes. An enhanced CH₄ yield was achieved in the photoreduction of CO₂ using flame annealed TiO₂ nanotubes, and isotope labeled experiments confirmed the reaction products to originate from the CO₂ reactant. Flame-annealed TiO₂ nanotubes formed in aqueous electrolyte (FANT-aq) yielded 156.5 μmol g_{catalyst}⁻¹.hr⁻¹ of CH₄, which is in the top tier of reported performance values achieved using TiO₂ as a stand-alone photocatalyst. This performance resulted because appreciable amounts of CH₄ were generated under visible light illumination as well. TiO₂ nanotubes exhibited CO₂ photoreduction activity up to a wavelength of 620 nm with visible light driven photocatalytic activity peaking at 450 nm for flame annealed TiO₂ nanotubes. Isotope labeling studies, using GC-MS and gas-phase FTIR, indicated photoreduction of ¹³CO₂ to ¹³CH₄. The detection of ¹³CO in the product mixture, and the absence of HCHO and HCOOH provides strong support for the photoreduction proceeding along a carbene pathway. The enhanced CO₂ photoreduction performance of FANT-aq is attributed to increased visible light absorption, square morphology, and the presence of rutile as the only crystalline phase with (110) as the dominant plane.

Keywords: solar fuel; carbon dioxide; mass spectrometry; DRIFTS; semiconductor photocatalysis

1. Introduction

The alarming rise of CO₂ concentrations in the atmosphere due to ever-increasing reliance of mankind on fossil fuels has intensified research to develop clean and carbon-neutral energy systems [1]. Numerous approaches such as CO₂ capture and storage [2], conversion of CO₂ into valuable products (e.g. cyclic carbonates and polycarbonate-polyols) [3], and microbial binding of CO₂ [4] have been proposed for fixation of CO₂ in extended time scales. The geological storage

of CO₂ is an energy intensive approach, which is less promising due to the inherent risk of sudden leakages, huge energy requirements and acidification of seawater. The photocatalytic conversion of CO₂ into light hydrocarbons using sunlight as a source of energy and water as a source of electrons and protons is an enticing approach to control carbon emissions. Since the discovery of photoelectrochemical CO₂ reduction on GaP by Halmann in 1978 [5] and subsequent work on the photocatalytic reduction of CO₂ in aqueous suspensions of WO₃, TiO₂, CdS and ZnO [6], several semiconductor photocatalysts have been explored for CO₂ activation. However, none of these semiconductors meet the requirements for efficient and durable CO₂ reduction. Among various semiconductor materials TiO₂ has gained wide consideration due to its non-toxic nature, wide abundance, durability under extreme conditions, and appropriate band-edge positions for CO₂ reduction. The dominance of TiO₂ in the field of semiconductor-mediated artificial photosynthesis is such that H. Garcia and colleagues authored a review article in 2013 titled *Photocatalytic CO₂ Reduction using Non-Titanium Metal Oxides and Sulfides* and still found non-TiO₂ materials to be “notoriously inefficient” [7]. However, TiO₂ possesses a wide bandgap of 3.0-3.2 eV that restricts optical absorption to photons in the ultraviolet (UV) spectral range, where only a tiny fraction (~ 5 %) of solar energy resides. Moreover, recombination losses are particularly pernicious for the reduction of CO₂ to fuels which involves 6-8 electron transfer steps [8].

Bandgap engineering using different schemes, e.g. doping with metals and non-metals, photosensitization with low band gap semiconductors as well as metal complexes, and composite formation with other semiconductors and carbonaceous materials, have been explored to improve visible light absorption in TiO₂. However, the yield of hydrocarbon reaction products has not exceeded a few micromoles per unit mass of catalyst. Flame annealed titania received significant attention in the early 2000s as a method to improve the visible light responsivity of TiO₂ through the introduction of defects and dopants [9-13]. In a highly cited but contentious study, S.U.M. Khan and colleagues reported on highly efficient water-splitting using flame annealed TiO₂ thin films in the journal *Science* in 2002 [9]. The results of these studies were challenged on the basis of spectral mismatch between the unfiltered Xe arc lamp used as the illumination source and the spectrum of terrestrial sunlight, potentially unphysical mechanisms used to explain the observed enhancement, and problems with the reproducibility of the reported results [14]. Consequently, this line of research was not widely pursued. Recently, there has been a resurgence of interest in

“black TiO₂”, which is a defect-rich form of reduced titania exhibiting visible light absorption over a broad spectral range, particularly for photoelectrochemical water-splitting [15-20].

The TiO₂ nanotube array structure affords the tremendous advantage of orthogonalization of the light absorption and charge separation processes [21-24]. The nature of anodic synthesis is such that the length of the nanotubes can be made as large as millimeters while the nanotube wall-thickness remains in the 5 – 30 nm range [25]. Thus, the nanotubes can be longer than the penetration depth of absorbed radiation while the wall-thickness of the nanotubes can be of the order of the carrier retrieval length (diffusion length + drift length due to surface band-bending [26-29]) such that a majority of the photogenerated carriers are able to reach the nanotube surface before recombination and/or trapping, and react with adsorbed reactants or electrolyte ions [30]. For this reason, one-dimensional TiO₂ nanostructures constitute some of the highest performing nanomaterial architectures for CO₂ reduction with reported CH₄ generation rates as high as 3.7 mL g⁻¹ hr⁻¹ [31, 32]. Typically, the TiO₂ nanotubes are decorated with monometallic or bimetallic co-catalyst nanoparticles (NPs) containing at least one noble metal such as Pt, Pd, Rh, Ru, Au, Cu, CuPt, ZnPd, AuCu, etc [33-38]. The presence of the noble metal assists in electron-hole pair separation and reduced recombination through the introduction of surface band-bending, produces favorable shifts in the flatband potential of the photocatalyst for CO₂ reduction, introduces new adsorption modes for CO₂ adsorption, generates plasmonic enhancement (for Ag and Au containing systems), and promotes phonon-driven catalysis through a coupling of the vibrational modes of the metal to those of organic adsorbates. Yet, the presence of noble metals increases costs dramatically and reduces the possibilities of scale up and commercial deployment. Many metal co-catalysts are also vulnerable to poisoning by reaction products or intermediates [39, 40].

In 2015, we reported on an unusual morphological transition from cylindrical nanotubes with circular or ellipsoidal cross-sections to jar-shaped nanotubes with square cross-sections that resulted from flame annealing of anodically formed TiO₂ nanotubes [23]. This morphological transition was accompanied by other unusual features such as the reduction in carrier density in the nanotubes by over an order of magnitude and a significant negative shift in the flat band voltage. In photoelectrochemical measurements in 1 M KOH, the flame annealed TiO₂ nanotubes (FANTs) outperformed low temperature annealed anatase-phase nanotubes (LANTs) and high temperature furnace-annealed dominant rutile-phase nanotubes (HANTs) by a factor of three to

five [23]. Herein, we report on the CO₂ reduction performance of FANTs as a stand-alone photocatalyst without any noble metal co-catalysts.

Phase pure rutile and mixed phase (rutile and anatase) square shaped TiO₂ nanotube arrays are formed by flame annealing, and an enhanced photoreduction performance is demonstrated for the photoreduction of CO₂ to CH₄ in simulated solar light and visible light alone (without any ultraviolet component) conditions. Flame annealed TiO₂ nanotubes with square-shaped pore morphologies were synthesized by electrochemical anodization in ethylene glycol based electrolyte (FANT-eg) and water based electrolyte (FANT-aq) followed by elevated temperature (750 °C) flame annealing. The CO₂ photoreduction performance of flame annealed TiO₂ nanotubes was compared to low temperature annealed nanotubes as synthesized in ethylene glycol based electrolyte (LANT-eg) and water based electrolyte (LANT-aq). While our isotope labelling experiments using gas chromatography with a mass spectrometric detector (GC-MS) and gas-phase Fourier transform infrared spectroscopy (FTIR) confirmed photoreduction of CO₂ to CH₄, we also performed systematic control experiments to verify the same. The importance of this work originates from the demonstration of bare TiO₂ nanotubes (*i.e.* without functionalization, intentional doping, *etc.*) formed using a simple solution-processing method, as efficient catalysts for the photoreduction of CO₂ to CH₄.

2. Materials and Methods

2.1 Materials

Ammonium fluoride (> 98 %), aqueous hydrofluoric acid (49 %), ethylene glycol, EG (> 99 %) and acetic acid (> 99 %) were obtained from Fisher Chemical and used in their as-received form without any further purification. De-ionized water was used throughout study, and all other solvents were of HPLC grade. Titanium Foil (99 %, 0.89 mm thickness) was procured from Alfa Aesar. Ti foil was cut into 1 cm x 2.5 cm pieces and washed by sonication in water, methanol and acetone each for 10 min to remove any organic/inorganic contaminant. ¹²CO₂ was of 99% purity and was obtained from Praxair (Canada). ¹³CO₂ of 99 % purity was obtained from Cambridge Isotope Laboratories, Inc. (USA).

2.2 Synthesis of TiO₂ nanotube arrays

Ethylene glycol (EG)-based organic electrolyte and water-based electrolyte were the two different recipes used to anodically form two different types of TiO₂ nanotubes. The EG-based electrolyte

contained 0.3 wt % NH_4F and 4 % v/v of deionized water. The water-based electrolyte contained 4 % v/v of HF and 8% v/v of acetic acid. The anodization process using water-based electrolyte was performed at room temperature in a two-electrode electrochemical cell using a graphite cathode at an applied voltage of 15 V. Anodization using EG-based electrolyte was also performed under identical conditions except that the applied voltage between the Ti anode and graphite cathode was maintained at 30 V. The obtained TiO_2 nanotube arrays using aqueous and EG based electrolyte were annealed in air at 450 °C for three hours and denoted as LANT-aq (low temperature annealed nanotubes prepared in aqueous medium) and LANT-eg (low temperature annealed nanotubes in ethylene glycol), respectively. Flame annealing was performed at high temperature (~ 750 °C) using a propane torch for about 2 minutes, and the resulting flame annealed nanotubes are called FANT-aq (flame annealed nanotubes prepared in water-based electrolyte) and FANT-eg (flame annealed nanotubes prepared in EG-based electrolyte).

2.3 Characterization

The nanoscale morphologies of the TiO_2 nanotubes were imaged using a field emission scanning electron microscope (FESEM, Hitachi-NB5000). X-ray diffraction (XRD) was performed using a glancing angle configuration in a Bruker D8 Discover instrument with a sealed $\text{Cu K}\alpha$ X-ray source (40 kV, $\lambda = 0.15418$ nm). Raman spectroscopic data was collected using a Nicolet Almega XR Raman Spectrometer with an incident laser wavelength of 532 nm and at an incident power of 24 mW. High-resolution transmission electron microscopy (HR-TEM) imaging to investigate fine morphological features was performed using a JEOL 2200 FS TEM at an acceleration voltage of 200 kV. Optical characterization was performed using a Perkin Elmer Lambda-1050 UV-Vis-NIR spectrophotometer equipped with an integrating sphere accessory. X-ray photoelectron spectra (XPS) for determining oxidation state and surface chemical composition of materials was acquired using an Axis-Ultra (Kratos Analytical) instrument equipped with monochromatic $\text{Al-K}\alpha$ source (15 kV, 50 W) and photon energy of 1486.7 eV under ultrahigh vacuum ($\sim 10^{-8}$ Torr). The binding energy of C1s core level ($\text{BE} \approx 284.8$ eV) of adventitious hydrocarbon was used as a standard to assign the binding energies of other elements. The raw data was deconvolved into various peak components using CasaXPS and later plotted in Origin 8.5. Brunauer–Emmett–Teller (BET) specific surface area measurement of the nanotubes, after being scrapped off from the Ti foil, was performed using an Autosorb iQ device. For BET measurement, nitrogen gas was used, degassing was performed at 350 °C and surface area was measured at -193 °C. To determine the presence of

Ti³⁺ and O²⁻ species, X-band continuous wave electron paramagnetic resonance (EPR) spectra of materials were recorded using a Bruker model E-580 (EMXnano) spectrometer (Germany) equipped with an Oxford CF935 helium flow cryostat. For the measurement, sample was scratched from Ti foil, charged in quartz tubes covered with air tight lids and EPR spectra were collected at 100 K using liquid nitrogen. Time-resolved photoluminescence (PL) data, was obtained by using 2-photon fluorescence lifetime imaging microscopy (FLIM). The excitation was by a femtosecond Ti:sapphire laser at a wavelength of 750 nm. Imaging was performed by using Zeiss LSM 510 NLO multi-photon microscope equipped with a FLIM module, which comprised of a Hamamatsu RS-39 multichannel plate detector, a filter wheel, and a Becker Hickl Q5 SPC730 photon-counting board.

2.4 Photocatalytic CO₂ reduction experiments

CO₂ photoreduction experiments were performed in a cylindrical reactor with a transparent quartz window, and an internal volume of 32 mL as described in our earlier reports [32, 36, 41]. Single pieces of TiO₂ nanotube array photocatalyst with an active area of 1 cm x 2 cm were placed inside the reactor, and a few droplets of water were placed in the reactor beside the catalyst without direct contact with the catalyst. Then the reactor was closed, and purged with CO₂ to remove any other gases using a two valve system, followed by pressurizing the reactor (housing the photocatalyst and water droplets) with 50 psi of CO₂. The photoreactor was heated to ~ 80 °C using a hot plate to convert the water droplets in the reactor into water vapor, and the photocatalyst was irradiated using the collimated AM 1.5G output of a Newport Class A solar simulator having an intensity of 100 mW cm⁻² on the photocatalyst surface at a distance of 32 cm from the light source. In order to investigate visible light induced photocatalysis, experiments were also performed wherein the catalysts were respectively illuminated using a 50 W LED lamp (maximum intensity around 510 nm) with filtered out UV light, and the same with a 650 nm high pass filter. In order to understand the wavelength dependence of photocatalytic activity, monochromatic LEDs of different wavelengths (400 nm, 450 nm, 500 nm and 620 nm), each with an output power intensity of 10 mW cm⁻² were used for irradiating the samples. After 2 hr of irradiation the reactor gas samples were analyzed using gas chromatography (GC model: SRI 8610C Gas Chromatograph) by injecting samples into the sample loop (1 mL) of the GC using simple Swagelok piping. The GC was equipped with a 10' HayeSep D 1/8" packed column, a thermal-conductivity detector (TCD), and a flame ionization detector (FID). Gases were eluted from the column isothermally at

85 °C for 10 min. Helium was used as the carrier gas and its flow rate through the column was maintained at 25 mL min⁻¹. Isotopic labelling experiments were performed using ¹³CO₂ to verify the origination of methane from photocatalytic reduction of CO₂. The obtained reaction product containing ¹³CH₄ was analyzed with gas chromatography-mass spectrometry (GC-MS) using an Agilent 7890A GC/MS instrument. Gas phase FTIR analysis (for detection of ¹³CH₄) was performed using a Magna System 750 FTIR, equipped with an IR source and detector (MCT/B). The FTIR system had a 4.8 meter multiple bounce gas cell (Infrared Analysis Inc. Anaheim USA, Model G-2-4.8-PA-BA-AG), and was evacuated to 100 mTorr and backfilled with dry argon (UHP 5.0 Praxair). This procedure was repeated three times then the gas cell was evacuated to 100 mTorr and a background acquired. The background spectrum was saved and used for subsequent data collection. Gas from the photoreactor was sampled directly from the reactor outlet port into a 0.25 L Tedlar bag. The sample was introduced directly into the gas cell by connecting the Tedlar bag valve to the gas cell valve. The sample spectrum was acquired with 400 Torr gas pressure inside the gas cell.

2.5 Optical simulations of nanotube arrays

Optical properties of the LANT and FANT-eg structures were investigated using Lumerical FDTD simulation software. LANT structures were simulated as nanotubes with circular cross-sections with inner and outer radii of 40 and 70 nm respectively, and height of 300 nm. Similarly, FANT-eg structures were simulated as nanotubes also of height 300 nm but with square cross-sections. The simulations were performed for both combinations of individual nanotubes in vacuum. Near-field, and far-field profile and frequency monitors were utilized to capture scattering and absorption cross sections, electric field intensity profiles, Poynting vector distributions as well as reflection and transmission spectra. Material compositions of rutile, anatase, and mixed rutile (42 %) - anatase (58 %) TiO₂ in LANT and FANT-eg structures were simulated using the appropriate refractive index data as obtained via ellipsometry. Refractive index data corresponding to the anatase TiO₂ were obtained from Siefke et al.[42] The effective medium approximation for the mixed-phase materials were determined via Bruggeman's model, labelled as eq. (1)

$$\sum_i \delta_i \frac{\sigma_i - \sigma_e}{\sigma_i + (n-1)\sigma_e} = 0 \quad (1)$$

where δ_i and σ_i are respectively the fraction and refractive index of each component, and σ_e is the effective conductivity of the medium. Lumerical's refractive index monitor was utilized to confirm

the structures were appropriately configured and identified by the software throughout the course of the simulation. The structures were illuminated by a light source incident at a normal angle from above with a bandwidth range of 350–800 nm. Snapshots of the electric field intensity profiles, and Poynting vector distributions were taken at specific wavelengths between 350–500 nm in 50 nm increments, and as viewed along different planes including the xy -, xz -, and yz -planes. The symmetry of the structures were considered by setting appropriate symmetric and anti-symmetric boundaries allowing for shorter simulation times, and accurate data aggregation.

3. Results and Discussion

3.1 Morphology, structure and chemical composition of regular- and flame annealed nanotubes

Fig. 1 is a schematic illustration of the flame annealing process. High-temperature annealing stimulates phase transformation from anatase to rutile which proceeds via a change square-shape morphological change (SEM image in inset of Fig. 1).

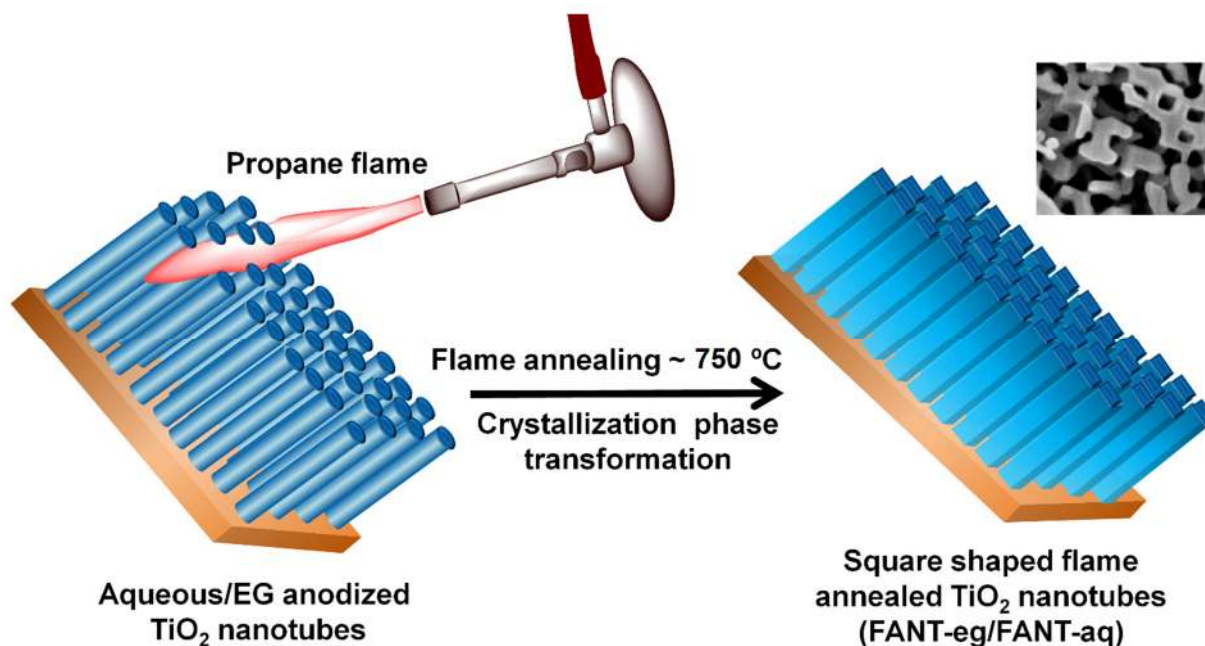


Figure 1. Schematic of synthesis of square shaped flame annealed TiO₂ nanotubes

The cross-section and top-view FESEM images of the TiO₂ nanotubes are shown in Fig. 2, from where their dimensions and distinguishing morphologies are evident. The average length of FANT-eg was found to be ~ 2 μm, while the same for FANT-aq was found to be 200 nm. The length of the nanotubes does not change significantly after flame annealing for both types of

nanotubes. However, the pores of FANT-eg nanotubes are transformed from circular to square shape. The average inner width of square pores of FANT-eg is 50 nm, while the same for FANT-aq is 80 nm. The average wall thickness values for FANT-eg and FANT-aq are 40 nm and 20 nm respectively. The average pore diameter is 80 nm for both LANT-eg and LANT-aq while the average wall thickness values for LANT-eg and LANT-aq are 20 nm and 15 nm respectively. To estimate the mass of the nanotubes, the fill fraction (f_{si}) of TiO_2 was determined as a fraction of the free space the nanotubes occupy.

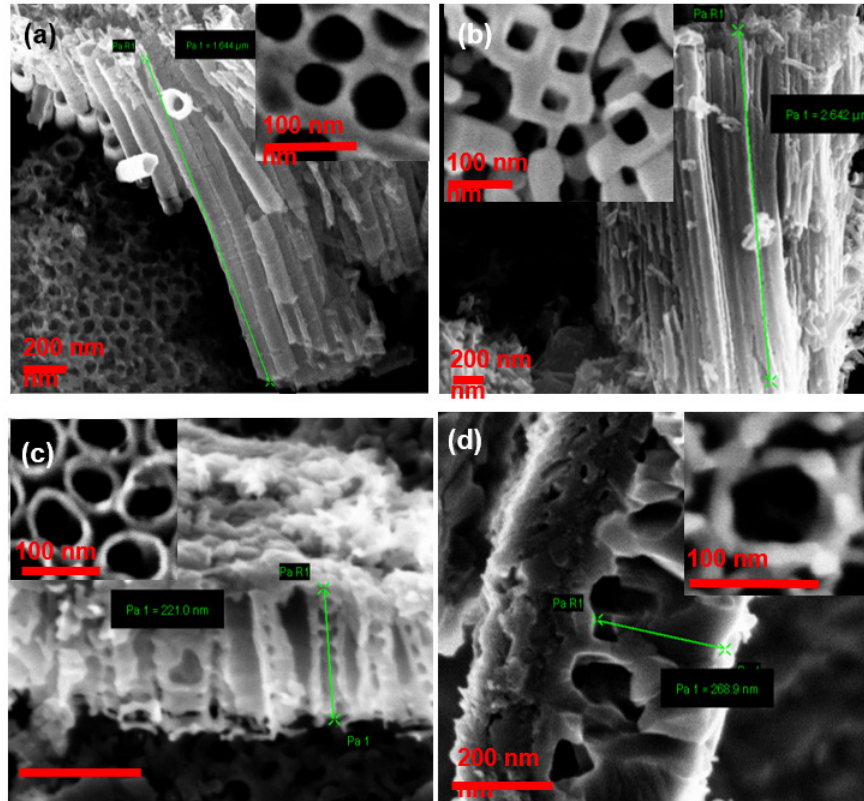


Figure 2. Cross-section FESEM images of LANT-eg (a), FANT-eg (b), LANT-aq (c) and FANT-aq (d). Insets are top-view FESEM images of the same.

The fill fractions for LANT-eg and LANT-aq were calculated using eq. (2) [43-45] and the fill fractions for FANT-eg and FANT-aq was calculated using eq. (3)

$$f_{sl} = \frac{\frac{2t}{R_0} - \left(\frac{t}{R_0}\right)^2}{\frac{2\sqrt{3}}{\pi} \left[1 + \left(\frac{s}{2R_0}\right)^2\right]} \quad (2)$$

$$f_{sl} = \frac{T_o^2 - T_i^2}{T_o^2} \quad (3)$$

In eq. (2), t is the average wall thickness and R_0 is the average radius of nanotubes, and s is the distance between adjacent nanotubes. In eq. (3), T_o and T_i are the widths of the outer and inner edges of the square-section of the nanotubes. Using the relevant dimensions of the nanotubes, fill fractions calculated using eqns. 2 and 3, and are displayed in Table 1. Using these fill fraction values, the mass of the nanotubes per unit area was also calculated, and is also shown in Table 1. While mass of the nanotubes were reliably calculated, our measured specific area of the EG anodized TiO₂ nanotubes was 583 m²/g, which is consistent with values reported in literature [46, 47]. Due to requirement of a large quantity of TiO₂ nanotube powder, we only performed BET surface area analysis on the longer EG anodized TiO₂ nanotubes. The specific areas of both, LANT-eg and FANT-eg, were the same.

Table 1 Measured dimensions, fill fraction, and mass per unit area of TiO₂ nanotubes used in this study

Nanotube type	Average nanotube length (μm)	Average nanotube pore diameter (nm)	Average nanotube wall thickness (nm)	Nanotube fill fraction	Nanotube mass per unit area (g cm ⁻²)
FANT-aq	0.2	80	20	0.106	8.97 × 10 ⁻⁶
LANT-aq	0.2	80	15	0.104	8.09 × 10 ⁻⁶
FANT-eg	2	50	40	0.497	4.01 × 10 ⁻⁴
LANT-eg	2	80	20	0.367	2.86 × 10 ⁻⁴

The fine structural features of the nanotube photocatalysts were determined with HR-TEM (Fig. 3). High temperature annealing promoted the formation of the thermodynamically stable rutile phase of TiO₂. Images of FANT-eg at 5 nm scale bar (Fig. 3a) show various domains of lattice fringes, having 0.33 nm and 0.21 nm inter-planar d-spacings associated with the rutile (110) and anatase (004) planes of TiO₂. The appearance of these planes reveals the presence of both

anatase and rutile phase TiO₂ domains in FANT-eg (Fig. 3a). The TEM image of TiO₂ nanotubes prepared using the aqueous recipe after flame annealing (FANT-aq) exhibits rutile phase alone; the 0.27 nm and 0.18 nm d-spacings in Fig. 3b respectively correspond to the (101) and (211) planes of rutile TiO₂. These phase transformations together with thermal stresses during flame annealing are likely responsible for the change in cross-section of TiO₂ nanotubes from circles to square shapes [23, 48]. LANT-eg and LANT-aq samples, annealed at 450 °C, show only the (101) and (004) planes of anatase phase TiO₂ with 0.35 nm and 0.25 nm d-spacing respectively (Fig. 3e and Fig. 3f). The presence of sharp diffraction rings in selected area diffraction pattern of FANT-eg show polycrystalline nature (Figure 3c). Diffraction rings corresponding to (101), (004), (200), (220) planes of anatase and (110), (211), (220), (002), (310) planes of rutile were observed in the SAED pattern of FANT-eg in Fig. 3c, which further confirmed the presence of both anatase and rutile phases of TiO₂ in the nanotubes. The SAED pattern of FANT-aq showed diffraction rings related to rutile phase TiO₂ alone (Fig. 3d). LANT-eg and FANT-aq displayed only anatase phase diffraction rings (Fig. 3g and Fig. 3h). The obtained results were fully consistent with XRD and Raman findings shown in Fig. 4 and Fig. 5, respectively.

A question that arises is what reason exists for the FANT-aq samples to be completely transformed from anatase into rutile by flame annealing while the FANT-eg samples are composed of a mixture of 52 % anatase and 48 % rutile. To answer this question, we must understand two aspects – one related to nanotube length and the other related to the anodization electrolyte. A higher annealing temperature promotes the anatase-to-rutile phase transition. The nanotubes grown in aqueous electrolyte (LANT-aq) are relatively short (0.2 μm nanotube length as indicated in Table 1) and the flame annealing process, which directly provides heat to the top surface of the nanotubes, is easily able to generate similarly high temperatures at the bottom of the nanotubes as it does at the top surface (small temperature gradient). On the other hand, the nanotubes grown in EG electrolyte are 2 μm long (Table 1) and there is a much higher chance of a temperature gradient persisting that would prevent the bottom parts of the nanotubes from reaching the temperatures generated by flame annealing at the top surface. Secondly, it is well known that nanotubes formed by anodization in EG-based electrolytes possess a higher amount of embedded fluoride ions [49]. Further, it is well-established that the incorporation of fluoride ions retards the anatase-to-rutile phase transformation due to which the FANT-eg samples retain a significant anatase fraction [49].

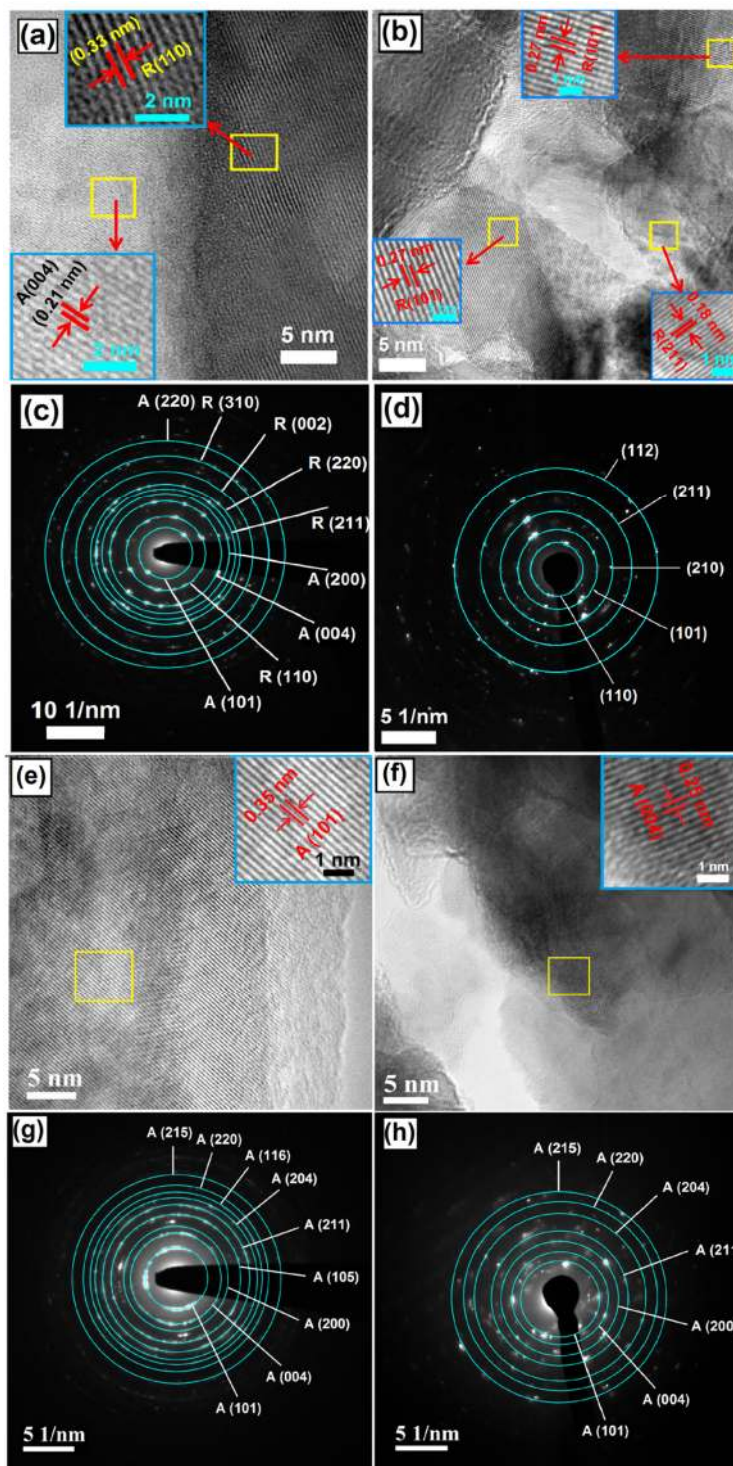


Figure 3. HR-TEM images showing fringe patterns and 2d spacing of FANT-eg (a), FANT-aq (b), LANT-eg (e) and LANT-aq (f); SAED patterns of FANT-eg (c), FANT-aq (d), LANT-eg and (g) LANT-aq (h).

For further confirmation of these phases, we analyzed the samples using XRD. For FANT-aq, the XRD pattern (red curve in Fig. 4) showed phase pure rutile, indicated by a dominant (110) peak at 27.4° (JCPDS No. 21-1276) while FANT-eg (blue curve in Fig. 4) showed the rutile (110) peak at 27.4° (JCPDS No. 21-1276) in addition to anatase (101) peak at 25.2° (JCPDS No. 21-1272), which demonstrates the presence of both anatase and rutile phase TiO_2 . The same XRD curve of FANT-eg is shown again in Fig. 4b, to highlight the presence of both anatase and rutile phases. The percentage of rutile phase in the anatase and rutile mixture in FANT-eg was calculated using eq. (4) [50] by measuring intensities of the most intense anatase (101) and rutile (110) peaks, and was found to be 42.72 %.

$$R = \frac{I_R}{I_R + 0.884I_A} \quad (4)$$

In eq. (4), R is the rutile percentage while I_R and I_A are the intensities of rutile and anatase peaks respectively. The optimum rutile percentage for obtaining the best photocatalytic performance has been previously reported to be between 20 and 40 % [51, 52]. Therefore, XRD data suggests close to optimum rutile phase content in FANT-eg samples. XRD patterns of LANT-eg (green curve in Fig. 4) and LANT-aq (black curve in Fig. 4) exhibit regular anatase peaks, which conform to the relatively low temperature annealing condition (*i.e.* 450°C) that promotes the formation of phase pure anatase. Grain sizes of the nanotubes varied with annealing temperature as well, and were calculated using the Scherrer equation, shown as eq. (5) below:

$$S = \frac{K\lambda}{\beta \cos\theta} \quad (5)$$

In eq. (5), S is the mean size of crystalline domains, K is a dimensionless shape factor (assumed as 1), λ is the X-ray wavelength which is 0.154 nm (Cu $K\alpha$ source), β is the peak width at half of the maximum intensity in radians, and θ is the Bragg angle. β was obtained using Lorentzian fits of the anatase (101) and rutile (110) peaks, as shown in Figs. S2 (a, b, c and d). The obtained crystallite grain sizes are listed in Table 2. FANT-eg nanotubes show the largest crystallite size for both anatase (36.17 nm) and rutile phase (41.66 nm).

The Raman spectra (Fig. 5a) of FANT-eg and LANT-eg are characterized by peaks at 141 cm^{-1} [43], with a higher peak intensity in FANT-eg due to contributions from both the anatase Eg and rutile B1g Raman active modes [53, 54]. Other Raman active modes of lower intensity are assigned to anatase. The Raman spectrum (Fig. 5b) of FANT-aq is characterized by an intense

peak at 141.1 cm^{-1} , which we attribute to rutile B1g by correlating with XRD and TEM data for the nanotubes. A similar peak, although slightly blue-shifted, appears in the Raman spectrum (Fig. 5b) of LANT-aq, which we attribute to the anatase Eg mode. Distinct Raman active modes, corresponding to rutile Eg and A1g, as well as a band corresponding to a multi-phonon processes, are also observed in the Raman spectra of FANT-aq [55]. Lower intensity anatase peaks B1g and Eg, appear in the Raman spectra of LANT-aq. Phonon lifetimes (τ) were calculated using the time-energy uncertainty relation (eq. 6) [56] for the Eg mode in the Raman spectra of the nanotubes.

$$\frac{1}{\tau} = \frac{\Delta E}{\hbar} \quad (6)$$

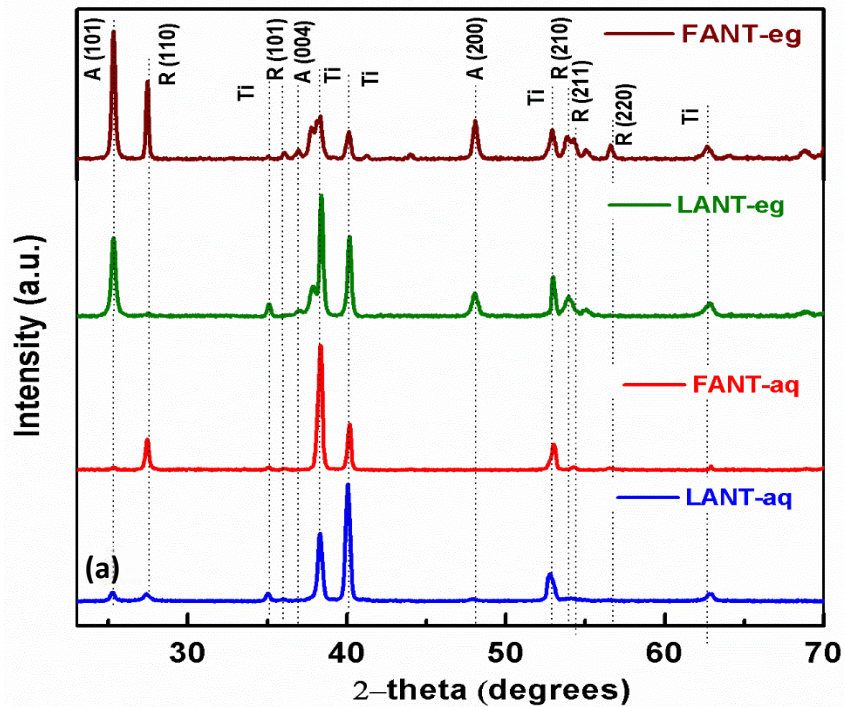
In eq. (6), ΔE is the FWHM, which was obtained from Lorentz fits of Eg peaks of the nanotubes, as shown in Fig. S3 (a, b, c and d); $\hbar = 5.3 \times 10^{-12} \text{ cm}^{-1} \cdot \text{s}$, and τ is the phonon lifetime. Values of phonon lifetimes of the nanotubes are listed in Table 2.

Table 2. Crystallite grain sizes of nanotubes, phase percentage, positions and widths of the Raman Eg modes, phonon lifetimes of the nanotubes, and $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio

Nanotube type	Crystallite size, anatase (101) (nm)	Crystallite size, rutile (110) (nm)	Crystalline Phase	Raman Peak position (cm^{-1})	Raman FWHM (cm^{-1})	Phonon lifetime (ps)	$\text{Ti}^{4+}/\text{Ti}^{3+}$
FANT-aq	-	36.18	100 % Rutile	141.23	11.09	0.48	12.67
LANT-aq	31.45	-	100 % Anatase	141.14	11.24	0.47	9.72
FANT-eg	36.17	41.66	100 % Anatase	141.11	11.24	0.47	8.91
LANT-eg	29.36	-	42 % Rutile 58 % Anatase	141.85	14.36	0.37	9.46

The optical properties of regular and flame annealed nanotubes were examined with diffuse reflectance UV-Vis spectroscopy (Fig. 6). The UV-Vis absorption spectrum of LANT-aq (black curve in Fig. 6) showed a sharp band edge at 386 nm characteristic of the anatase bandgap (3.2 eV) which was redshifted to 410 nm in FANT-aq (red curve in Fig. 6). This characteristic of the bandgap of rutile (3.0 eV), and occurs due to the anatase to rutile phase transition previously explained. On the other hand, the band-edge for both LANT-eg and FANT-eg samples is at *ca.* 400 nm, as explained below. Additionally, a broad hump around 450 nm was also observed for LANT-aq which is known to originate from defects and midgap trap states in anatase TiO_2 [57-

59]. Another broad absorption band extending from 550 to 750 nm is likely due to metallic d-orbital transition of the Ti foil substrate [60]. Both the FANT-eg and FANT-aq samples exhibited a monotonically increasing longer wavelength absorption which is attributed to the Drude absorption of conduction band electrons in TiO₂ [61]. The non-monotonic extended visible absorption of FANT-eg (cyan curve in Fig. 6) and LANT-eg (blue curve in Fig. 6) are due to the localized excitation of Ti³⁺ states vis $3d \rightarrow 3d$ transitions [62]. The Ti³⁺ states are created due to relatively more reducing conditions during anodic synthesis in organic electrolytes [63] which are not completely oxidized even after thermal annealing. FANT-aq showed a band tail around 410 nm. PL lifetime decay data (Fig. S3) for FANT-eg and LANT-eg were fitted to single exponential decay curves while the data for FANT-aq was fitted to bi-exponential decay curve, and the data for LANT-aq was fitted to a single exponential decay. FLIM data indicated an increase in PL lifetime because of flame annealing of the nanotubes. 2-photon fluorescence images are shown in Fig. S4, where it can be observed that the flame annealed nanotubes (FANT-eg and FANT-aq) are more fluorescent than the non-flame annealed nanotubes (LANT-eg and LANT-aq). The higher fluorescence intensity and longer lifetimes are due to suppressed non-radiative recombination processes [64, 65].



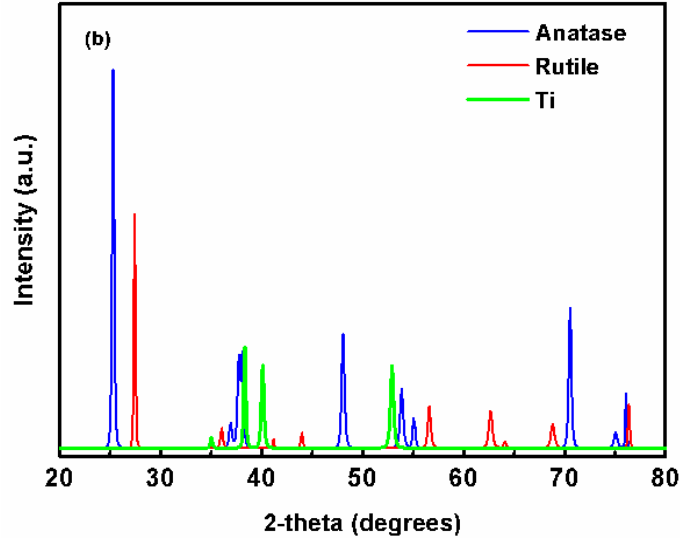


Figure 4. (a) Glancing angle XRD patterns of FANT-eg, LANT-eg, FANT-aq, and LANT-aq (b) Glancing angle XRD pattern of FANT-eg specifically, highlighting the mixed phase nature by separating the signal from each phase.

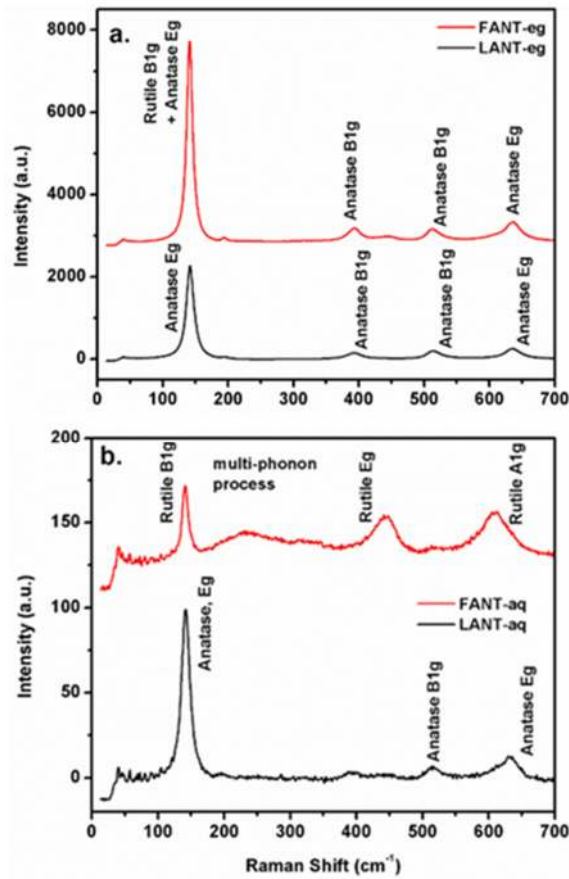


Figure 5. Raman spectra of: (a) FANT-eg, and LANT-eg; and (b) FANT-aq, and LANT-aq.

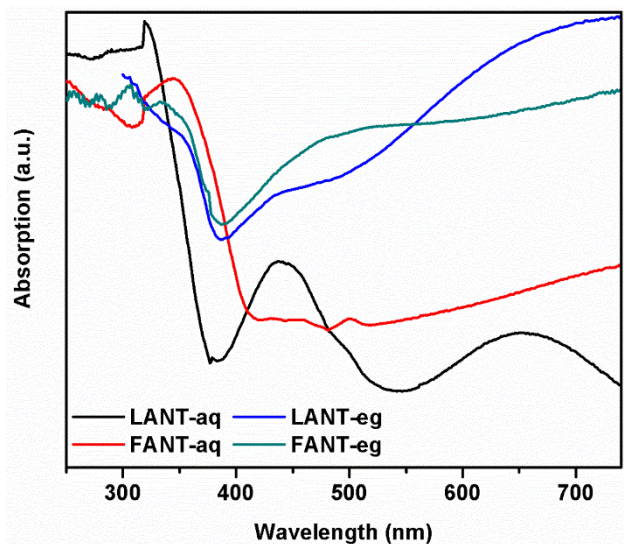


Figure 6. UV-Vis spectra of the nanotubes

The surface chemical composition and presence of defects were validated using X-ray photoelectron microscopy. Elemental survey scans (Fig. S5) of all nanotubes samples exhibit peaks corresponding to $Ti2p$ and $O1s$ (Fig. 7). High resolution XPS spectra of all TiO_2 nanotubes in $Ti2p$ region can be de-convolved into four peak components. The major peak components at binding energies of 458.6 eV and 464.4 eV were assigned to $Ti2p_{3/2}$ and $Ti2p_{1/2}$ core level transitions of Ti^{4+} [35, 66, 67]. Two minor peaks at lower binding energy, 457.88 and 463.3 eV, were attributed to $Ti2p_{3/2}$ and $Ti2p_{1/2}$ peak components of Ti^{3+} present in the form of lattice defects [68-70]. As anticipated, for FANT-eg nanotubes the ratio of Ti^{4+} to Ti^{3+} was found to be lowest (8.91, shown in Table 2) which suggests that flame annealing and phase transformation at higher temperatures facilitate the abstraction of some lattice oxygen that created oxygen vacancies and Ti^{3+} states. The presence of Ti^{3+} and oxygen defects creates defect levels below the conduction band which facilitate sub-bandgap electronic transitions [71-73]. The de-convolved HR-XPS spectra of all nanotubes in $O1s$ display two peak components at binding energy 528.8 and 531.6 eV (Fig. 7). The strong peak at 528.8 eV originated due to oxygen atoms bonded to Ti atoms (Ti-O-Ti) in TiO_2 lattice while the peak shoulder component at *ca.* 531.6 eV appeared due to the presence of non-lattice adventitious oxygen and surface -OH groups [74]. The peak intensity of the non-lattice bonded oxygen peak component was substantially larger for TiO_2 nanotubes prepared in aqueous medium in comparison to TiO_2 nanotubes prepared in EG solvent which

indicate that even after annealing some residual oxygen was present on the surface of aqueous nanotubes.

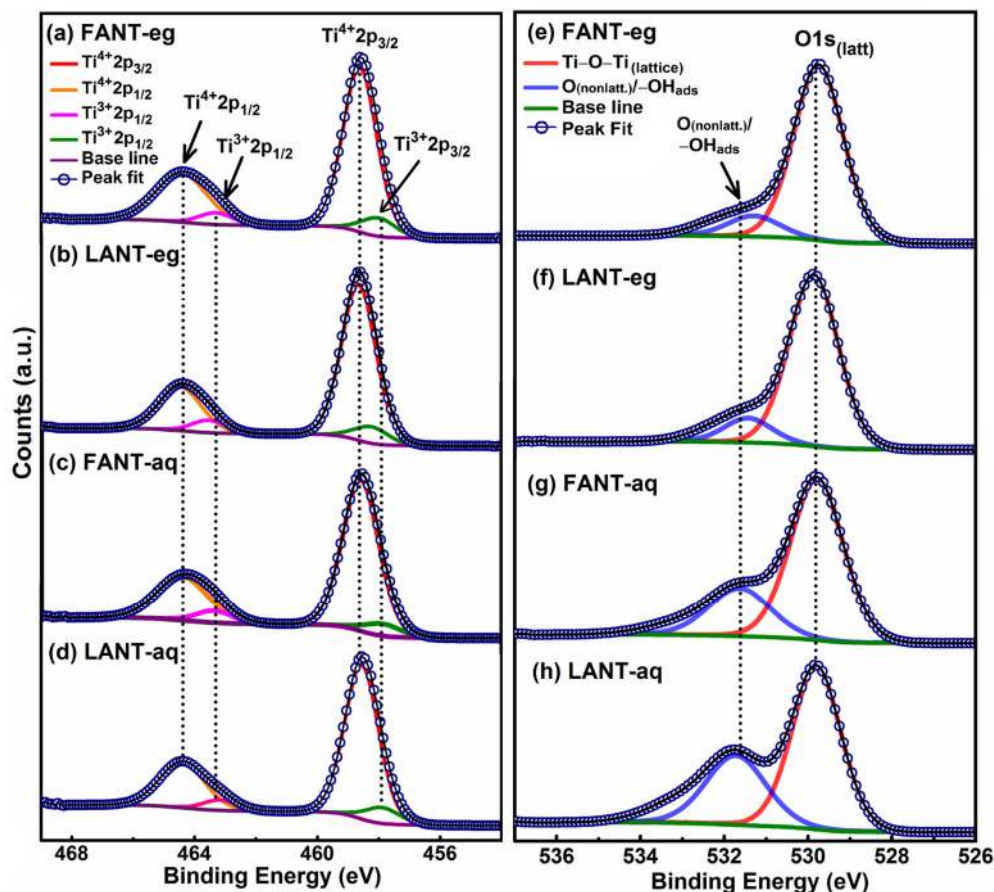


Figure 7. High resolution XPS spectra of FANT-eg , LANT-eg , FANT-aq and LANT-aq in (a-d) Ti $2p$ region and (e-h) in O $1s$ region respectively.

Since XPS provides only surface chemical information limited to 10 nm and elected photoelectrons may contribute to Ti^{3+} XPS signal due to reduction of Ti^{4+} species *via* high energy photoelectrons. Further, Ti^{3+} is vulnerable to oxidation under O_2 and can sustain for short time. So, to validate the presence of Ti^{3+} species and surface defects in bulk material, X-band EPR spectra of highly performing flame annealed EG based nanotubes (FANT-eg) was collected at 100 K under dark conditions. The low temperature EPR spectra of FANT-eg exhibits an intense Lorentzian signal at g value of 2.001. The EPR signal at $g \approx 2.001$ corresponded to O_2^- was observed due to reduction of surface adsorbed O_2 *via* surface Ti^{3+} species, indicates presence of plenty of Ti^{3+} species in the sample [67, 75-77]. In addition, a weak broad signal at g value of 1.973 confirms existence of Ti^{3+} species in the samples which was originated due to oxygen-

centered surface hole trapping sites during flame annealing process. The Ti^{3+} peak was broad which suggest distribution of coordination environment of surface centered radicals [17, 76, 78]. We have included this information in Figure S6 in ESI†. The EPR signal at $g = 4.266$ is said to derive from dopant species i.e. Fe^{3+} , V^{4+} , etc but might also originate from Ti self doping [79, 80].

3.2 CO_2 photoreduction performance of regular- and flame annealed TiO_2 nanotubes

The performance of the four types of titania nanotube samples was investigated for heterogeneous photocatalysis. Vapor phase CO_2 photoreduction experiments were performed using the solid phase TiO_2 nanotubes as the photocatalyst in the presence of CO_2 and water vapor as reactants under exposure to light from different sources for two hours. The photocatalytic CH_4 production per hour of reaction time, per unit mass ($\mu\text{mol g}_{\text{catalyst}}^{-1} \text{hr}^{-1}$) of catalyst is shown in Table 3. Fig. S7 in the supporting information shows the photoreduction performance for specific narrow spectral bands of FANT-eg and LANT-eg samples at an illumination intensity of 10 mW cm^{-2} . It is evident from Table 3 that under simulated solar light condition, flame annealed nanotubes exhibited extremely high CH_4 production rate ($156 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{hr}^{-1}$ for FANT-aq and $9.5 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{hr}^{-1}$ for FANT-eg). Under identical conditions the yields of CH_4 from CO_2 photoreduction were found to be $92 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{hr}^{-1}$ and $2 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{hr}^{-1}$ for LANT-aq and LANT-eg, respectively. Under illumination with a 50 W LED lamp light (maximum intensity at $\lambda_{\text{max}} = 510 \text{ nm}$) with a filtered out UV component, CH_4 yield with the flame annealed TiO_2 nanotubes dropped significantly for FANT-aq ($68 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{hr}^{-1}$) while it remained almost the same for FANT-eg ($9 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{hr}^{-1}$). The decrease in CH_4 yield for FANT-aq during illumination using the broadband visible LED lamp is in agreement with the UV-Vis spectrum of FANT-aq, which exhibited an absorption edge at 410 nm. Upon illumination with LED lamp light (with filtered out UV light) with a 650 nm long pass filter, the yield of CH_4 further decreased for all nanotube samples, as expected. Markedly higher photocatalytic CH_4 yields were observed with flame annealed TiO_2 nanotubes (FANT-eg and FANT-aq) than those with furnace annealed TiO_2 nanotubes (LANT-eg and LANT-aq). The observed CH_4 yields with the flame annealed TiO_2 nanotubes in this work exceed most reports with stand-alone TiO_2 catalysts, and are either comparable to or exceed CH_4 yields obtained with TiO_2 -based functionalized catalysts and nanocomposites [36, 81-90].

As mentioned earlier in this report, mass of the nanotubes is calculated by considering the nanotubes under a given irradiated geometrical area (or projected area to incident light), the fill

fraction of nanotubes and length of the nanotubes. Therefore, in addition to measuring CH₄ yield in $\mu\text{mol g}_{\text{catalyst}}^{-1} \text{hr}^{-1}$, the yield can be measured in $\mu\text{mol cm}^{-2}_{\text{illuminated area}}$, where the projected area is considered. The projected surface area of a photocatalyst determines the amount of non-concentrated solar energy that it is incident on it for potential transformation into chemical energy. CH₄ yields (Fig. S8) obtained using FANT-aq, LANT-aq, FANT-eg, and LANT-eg, were found to be 0.0014, 0.0007, 0.00383, and 0.0006 $\mu\text{mol cm}^{-2}_{\text{illuminated area}}$, respectively, under illumination of AM 1.5G, 100 mW cm⁻². Although our reported CH₄ yield appeared in nM.cm⁻² (or a small fraction of $\mu\text{mol g}_{\text{catalyst}}^{-1} \text{hr}^{-1}$), there are a few literature reports [91], which mention CH₄ yield per unit area, whereby the yields are similar or smaller than that reported by us. Upon initial inspection, it would seem that FANT-eg samples are now outperforming FANT-aq under this different metric; the reason for this disparity is due to the length of the nanotubes used (reported in Table 1). Generally, longer EG anodized nanotubes (LANT-eg and FANT-eg) absorb a larger fraction of incident light than aqueous nanotubes, and as a result, produce larger amounts of CH₄ per unit illumination area than the shorter nanotubes formed in aqueous electrolyte (LANT-aq and FANT-aq). Although the yield of CH₄ per unit mass was higher for FANT-aq, the CH₄ yield in terms of yield per unit area was higher for FANT-eg. While LANT-eg did not quite outperform LANT-aq in terms of the yield per unit area metric, the disparity between the two became much smaller.

While CH₄ is major product of CO₂ reduction, we also observed CO and trace amounts of C₂H₄ and C₂H₆ in our GC-MS and GC-FID based gas analysis (Fig. S10 and S11). In addition to gas phase experiments, our liquid phase CO₂ reduction experiments (described in the Supporting Information, and Fig. S12), proved the absence of reaction intermediates such as CO₃⁻, HCO₃⁻, HCOO⁻, *etc.* We also assessed re-usability/stability of catalysts, in which we found that FANT-aq and FANT-eg exhibited good stability, in that product yield (Fig S13, below) went down slightly and then thereafter remained constant.

In order to confirm CH₄ formation from the photoreduction of CO₂ and to rule out any possibility of carbon contamination, we performed isotope labeling experiments using ¹³CO₂ instead of ¹²CO₂ under identical reaction conditions. GC-MS (Fig. 8b) and gas phase FTIR analysis (Fig. 8a) of the gas evolved in the photoreactor after exposure of FANT-eg to the LED source in the presence of ¹³CO₂ and water vapor, confirmed the presence of ¹³CH₄. The GC-MS spectra (Fig. 8b) of reaction products showed an ion-chromatogram peak at *m/e* value of 17 for ¹³CH₄,

confirming that CH₄ was formed by photoreduction of CO₂. FTIR spectra (Fig. 8b) showed an isotope effect-induced shift in the C–H stretching mode from 3017 cm⁻¹ in ¹²CH₄ to 3010 cm⁻¹ indicative of the presence of ¹³CH₄ in the produced gas [92-94]. Similar peak shifts were observed for other IR active modes for ¹³CH₄, as shown in Fig. 8a. In addition to the isotope labeling study, we also performed a series of control experiments by: (i) exposing TiO₂ nanotubes in the reactor to light in presence of water droplets and CO₂ (without heat and therefore no water vapor); (ii) placing TiO₂ nanotubes in the reactor filled with CO₂ and water vapor only, without illumination (to verify the action of light); (iii) not using TiO₂ (or any catalyst), but exposing the reactor to light, with water vapor and CO₂ in it (to detect any methane impurities in the reactor); (iv) not using TiO₂ (or any catalyst) and water vapor, but by exposing the reactor with CO₂ to light and heat (to detect any methanation of carbon impurities in reactor); and (v) by exposing TiO₂ nanotubes in the reactor to light, with the reactor having water vapor but no CO₂ (to verify that CO₂ is an essential reactant for methane generation). In each of these control experiments, the CH₄ yield was negligibly low, implying that CH₄ was produced by CO₂ photoreduction in the presence of catalyst, water vapor (produced by heating), light and CO₂. In experiments with only heat and no light, with FANT-eg, CH₄ produced was explicitly low and the obtained CH₄ yield was subtracted from the total CH₄ yield, to calculate the total quantity of CH₄ produced in experiments with heat and light.

Table 3. CH₄ yield by CO₂ photoreduction using FANT-eg, LANT-eg, FANT-aq, and LANT-aq, as well as some comparisons to previous literature

Sample	Illumination Condition	CH ₄ yield per unit mass (μmol.g ⁻¹ .hr ⁻¹)	Reference
FANT-aq	AM 1.5G, 100 mW cm ⁻²	156.5	-
	50 W LED lamp*	67.9	-
LANT-aq	AM 1.5G, 100 mW cm ⁻²	92.0	-
	50 W LED lamp*	43.2	-
FANT-eg	AM 1.5G, 100 mW cm ⁻²	9.5	-
	50 W LED lamp*	8.8	-
LANT-eg	AM 1.5G, 100 mW cm ⁻²	2.0	-
	50 W LED lamp*	1.1	-
TiO ₂ Microspheres with 0.6 wt.% Pt Loading	Hg UV Lamp	2.0	[81]
Pd-TiO ₂ Particles	Light >310nm wavelength	0.4	[83]
CuO-TiO ₂ Hollow Spheres	Hg UV Lamp	2.0	[84]

TiO ₂ Nanoparticles	UV Light	0.6	[85]
Carbon Nanotube-Supported TiO ₂	15 W 365 nm UV Lamp	14.7	[95]
Graphene Supported TiO ₂	300 W Xe arc Lamp	27.4	[88]
TiO ₂ Nanoparticles	8 W Hg Lamp	9.5	[96]

*50 W LED lamp with max intensity 510 nm and UV filter

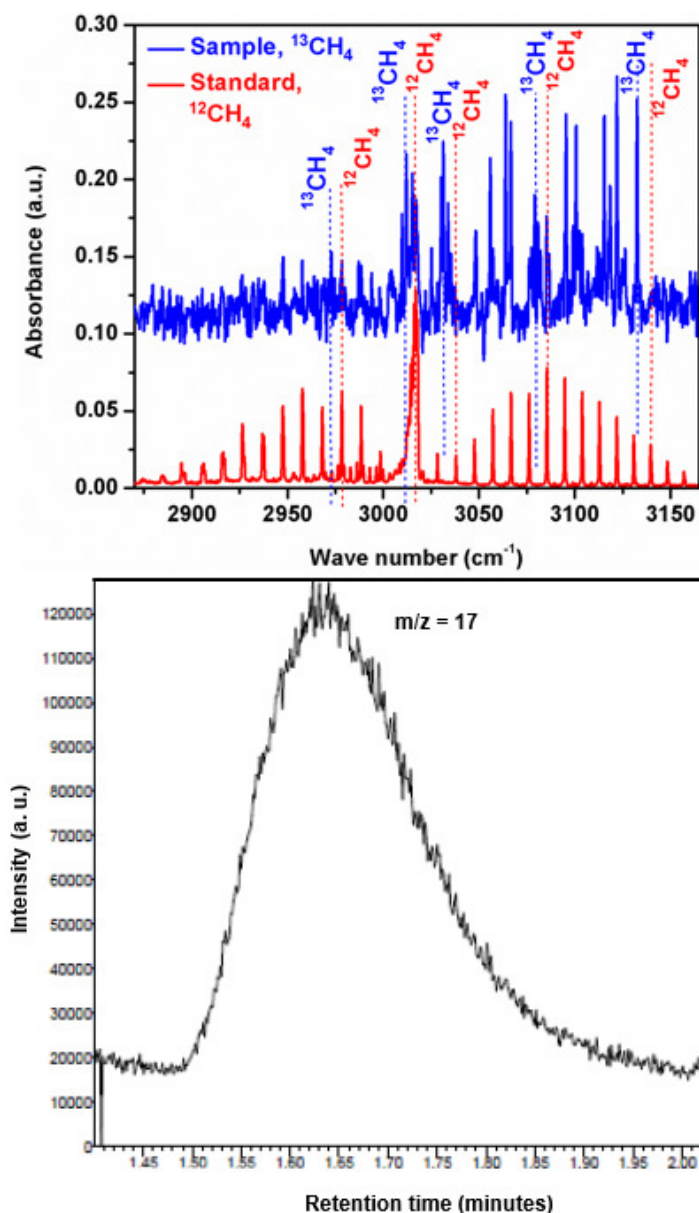


Figure 8. (a) FTIR spectra of gas sample generated by photoreduction of ¹³CO₂ using FANT-eg. Shifts to lower wavenumbers (between 7 and 10 cm⁻¹) of peaks in ν₃ bands of the gas sample, from ¹²CH₄ standard, confirms

presence of $^{13}\text{CH}_4$ as a product. (b) GS-MS ion-chromatogram at $m/e = 17$, confirming presence of $^{13}\text{CH}_4$ by photoreduction of $^{13}\text{CO}_2$.

3.3 Interaction of incident light with regular- and flame annealed TiO_2 nanotubes

A key question that arises is what effects relevant to photocatalytic action result from the differences in the structures and morphologies of the flame annealed titania nanotubes vs the regular furnace annealed nanotubes. One critical effect that is morphology and phase-dependent is the propagation of light and the concomitant spatial distribution of the electric field intensity in the photocatalysts. In order to investigate the effect of nanotube shape and phase content, we used Lumerical[®] to simulate the optical properties of the nanotubes, and the results are shown in Fig. 9 and in Fig. S8 in Supporting Information.

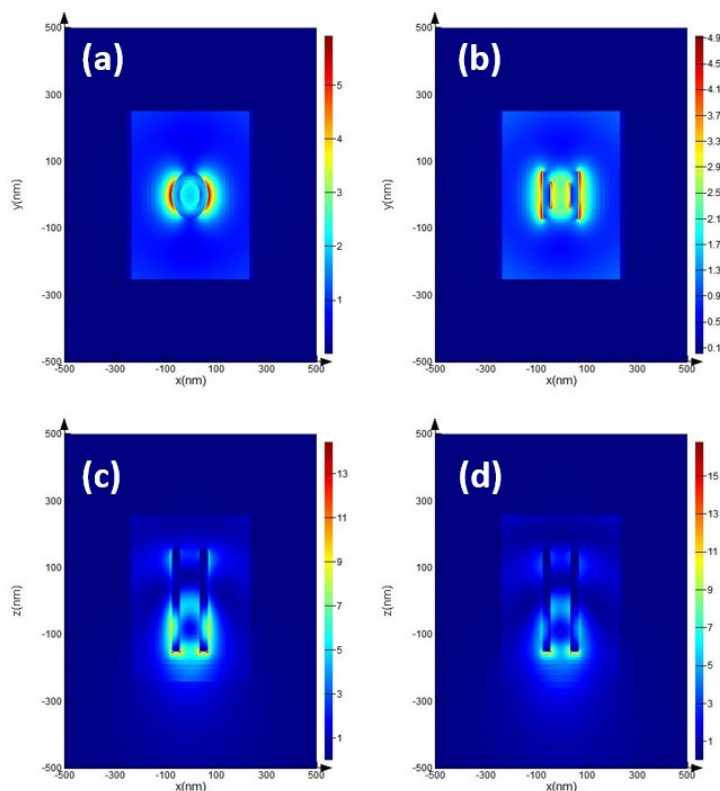


Figure 9. Poynting vector plots for (a) LANT and (b) FANT-eg for $\lambda = 450$ nm. Electric field intensity plots for (c) LANT and (d) FANT-eg for $\lambda = 400$ nm.

Fig. 9 indicates that the propagation of light is different in the LANT and FANT-eg samples. Areas with high local electric fields (hot spots) are particularly beneficial in photocatalysis. Since the nanotubes exhibited a peak visible light response at a wavelength of 450 nm as seen in Fig. S7, the Poynting vector plots of LANT and FANT-eg were examined at this

wavelength in the substrate plane. In Fig. 9a (LANT), hot spots are found on the outer surface of the nanotubes alone while in Fig. 9b (FANT-eg), hot spots are found on both the inner and outer surfaces of the nanotubes. The electric field intensities were examined at the optical band edge (400 nm) in the plane orthogonal to both the substrate and the optical polarization (Figs. 9c and 9d). In Fig. 9c, the extinction of the electric field due to absorption of incident 450 nm light in the nanotubes with circular cross-section is not complete as is evident from the higher field intensities observed close to the bottom of the nanotubes. On the other hand, more complete absorption of incident light is observed in the square nanotubes (Fig. 9d). The utilization of photons at the semiconductor band-edge is a loss mechanism in all solar energy harvesting devices, and our simulations demonstrate that square-shaped, mixed phase nanotubes (FANT-eg) absorb 400 nm band-edge photons more effectively than anatase phase nanotubes with a circular cross-section (LANT), and also result in a larger number of hot spots when irradiated with visible light.

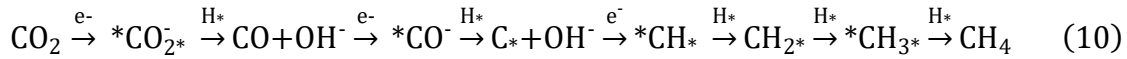
Fig. S9 (Supporting Information) shows the simulated absorption and scattering efficiency spectra for single nanotubes of the three different types investigated in this study. LANT-type nanotubes exhibit a strong scattering peak at a wavelength slightly lower than 400 nm (Fig. 98a) which manifests itself in the experimentally observed UV-Vis spectrum of the LANT sample (black curve in Fig. 6) as a strong dip in absorption at a wavelength slightly lower than 400 nm. Similarly, the strong scattering peak of FANT-eg type nanotubes seen in Fig. S9b at a wavelength slightly higher than 400 nm manifests itself in the experimentally observed UV-Vis spectrum of the FANT-eg sample (cyan curve in Fig. 6) as a strong dip in absorption at a wavelength slightly higher than 400 nm. Our simulations indicate that FANT-aq type nanotubes exhibit a broad, multi-peaked scattering feature in the 400-700 nm spectral range (Fig. S9c), which corresponds well with the large trough in the 400-700 nm spectral range in the experimentally observed UV-Vis spectrum of the FANT-aq sample (red curve in Fig. 6). It must be noted though, that the effects of Ti^{3+} states and free electrons on the absorption of the samples were not incorporated into the model used to simulate the optical properties of the nanotubes.

3.4 Mechanism of CO_2 reduction

In general, the photoreduction of CO_2 by one electron—which forms a bent $\text{CO}_2^{\bullet-}$ anion radical—is highly unfavorable due to repulsion between p orbitals, which necessitates a high reduction potential (−1.90 V). However, proton assisted reduction of CO_2 by multiple electrons and protons proceeds at lower applied reduction potentials. CH_4 formation from CO_2 by 8 electrons

and 8 protons needs only -0.24 V (*vs* NHE at pH 7). For the sustainable supply of electrons and protons, water must be oxidized to oxygen along with generation of electrons and protons needed for the photoreduction of CO_2 . Therefore, for efficient CO_2 photoreduction to methane, the position of the conduction band of the photocatalyst must be more negative than reduction potential of CO_2/CH_4 (-0.24 V *vs* NHE at pH-7) whilst the position of the valence band should be more positive than the oxidation potential of water ($\text{H}_2\text{O}/\text{O}_2$ $+0.82$ V *vs* NHE at pH-7 or $+1.23$ V *vs* NHE at pH 0). Therefore, the bandgap of the semiconductor should be higher than 1.23 eV in order to achieve CO_2 reduction and water splitting. Anatase phase of TiO_2 possesses a wide band gap of 3.2 eV with a conduction band position of -0.58 V *vs* NHE at pH-7 and valence band position of $+2.52$ V *vs* NHE at pH 7 [97, 98]. The position of the conduction band of rutile TiO_2 is 0.2 V lower than of anatase form with a bandgap value of 3.0 eV. Annealing of TiO_2 in oxygen deficient conditions can induce oxygen vacancies and Ti^{3+} states, which create subenergy levels below the conduction band [99]. These subenergy levels decrease the energy required for the excitation of electrons which is evident from the UV-Vis spectra in Fig. 6. For FANT-aq, flame annealing transforms anatase phase to pure rutile with a slightly lower band gap value (3.0 eV). The effective band gap is further reduced due to defects and subenergy levels, and therefore better light absorption characteristics and photocatalytic performance were observed with FANT-aq. However, for single phase rutile TiO_2 , the carrier recombination is faster than for TiO_2 containing a mixture of anatase and rutile phases [52]. Loss of carriers to recombination is somewhat mitigated by the thin walls of the water anodized FANT-aq resulting in their enhanced CO_2 photoreduction performance. In addition to the above phenomenon, the preferentially oriented rutile (110) in FANT-aq is a likely facilitator of enhanced CH_4 yield because, in such crystalline planes, fast hydrogenation of activated CO_2 occurs via the carbene pathway [100]. In FANT-eg, both anatase and rutile phases are present and expected to enhance CH_4 yield due to reduced recombination of photogenerated carriers. Fig. 10 illustrates the mechanism with FANT-eg, where both rutile and anatase phase co-exist. The synergetic enhancement of photocatalytic activity due to the presence of both anatase and rutile is well documented [52, 101, 102]; the energy difference between conduction bands of anatase and rutile TiO_2 causes photogenerated electrons in the conduction band of anatase TiO_2 to be transferred to the conduction band of rutile in mixed phase TiO_2 . There are, however, other literature reports that, on the basis of XPS, EPR and theoretical calculations, claim that anatase TiO_2 possesses low energy shallow traps (0.8 eV below the

conduction band of rutile) that cause electrons to move from rutile to anatase as well [102-104]. Holes can remain in the valence band of the same semiconductor or can move to valence band of rutile or anatase TiO₂ depending on the type of transition and energy state. Either due to transfer of electrons from anatase to rutile or vice versa, efficient separation of charge carriers in mixed phase TiO₂ was achieved. Furthermore, the presence of sub-energy levels just below the conduction bands made low energy transition feasible under visible light irradiation.



The photoreduction in presence of water vapor and CO₂ likely initiates by adsorption of the reactants (CO₂ and H₂O) on the TiO₂ surface followed by photo-induced activation by electron and hole transfer, respectively [90, 105]. Illumination creates charge carriers, the carriers are separated owing to the nanotube morphology (wall-thickness ~ carrier diffusion length), the holes in the valence band of TiO₂ dissociates water to protons and OH⁻ (which get converted into oxygen) (eq. 7-10). The protons, after accepting one electron from the conduction band, get transformed to atomic hydrogen (H^{*}), while the adsorbed CO₂ gets activated to CO₂^{-*} through electron transfer from TiO₂. The high majority carrier concentration in TiO₂ nanotubes (particularly those formed in EG electrolyte) indicated by the monotonically increasing Drude electron absorption in Fig. 6 is known to facilitate electron transfer and improve photocatalytic performance [106]. Through subsequent steps involving activated CO₂^{-*} and multiple H^{*}, CH₄ was formed as the final product. The transformation of CO₂ into CH₄ follows three pathways i.e. carbene pathway, formaldehyde pathway and carboxylate pathway [107, 108]. Based on previous EPR studies [109, 110], the methanation of CO₂ by the carbene pathway in the presence of H^{*} atoms and Ti³⁺ defects proceeds by formation of active surface carbon (*i.e.* C_{*}), which is converted into CH₄ as depicted in the reaction given in eq. (10). As evident from eq. (10), by-products such as formaldehyde, methanol and carboxylates (CO₃⁻, HCO₃⁻, HCOO⁻, *etc.*) are absent [98, 108-112] leading to the more selective formation of CH₄. This was confirmed by HPLC (Fig. S12) which failed to detect formaldehyde or formic acid in the reaction products. On the other hand, isotope labeled gas chromatography-mass spectrometry (GC-MS) confirmed the presence of ¹³C

following the photoreduction of $^{13}\text{CO}_2$. Since CO is a key reaction intermediate in eq. (10), the detection of CO (Fig. S10) strongly supports the carbene pathway as the mechanistic route for CO_2 photoreduction in our samples. The absence of any detectable H_2 can be explained from the less negative reduction potential of CO_2/CH_4 (-0.24 V vs NHE at pH 7) in comparison to H^+/H_2 (-0.42 V vs NHE at pH 7), which promotes formation of the more thermodynamically stable CH_4 as the product. Furthermore, the excess of CO_2 in reaction mixture ruled out possible recombination of H^* to form H_2 .

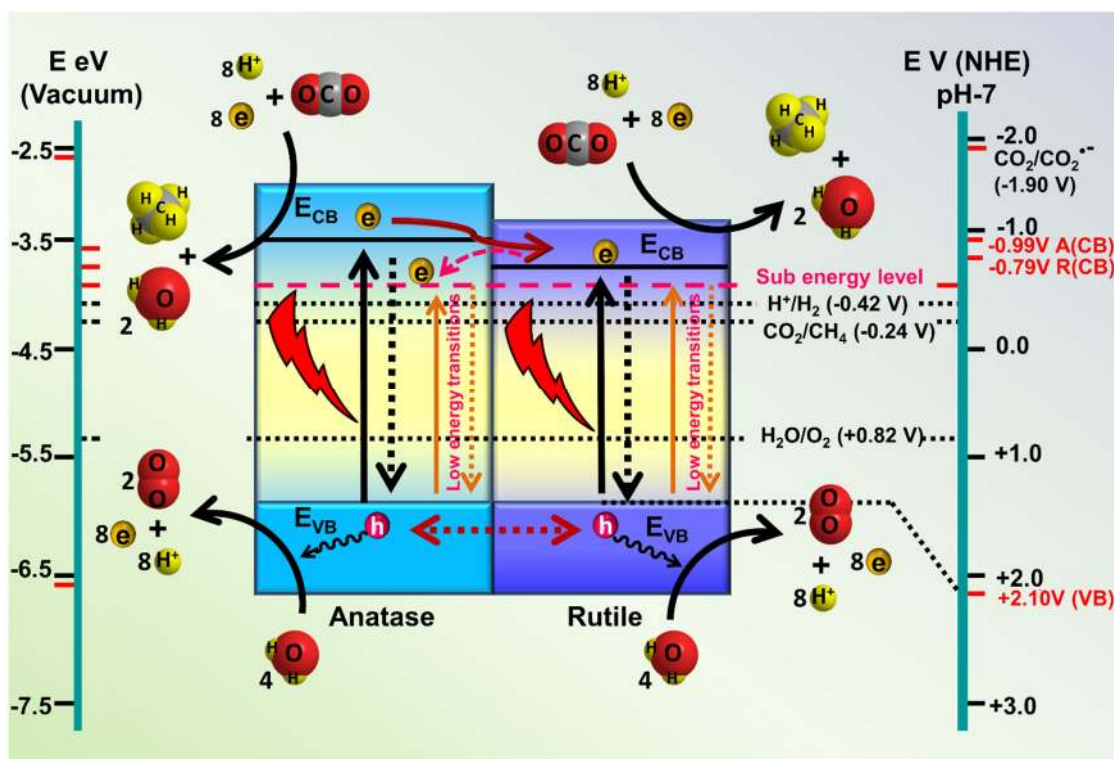


Figure 10. Plausible mechanism of photoreduction of CO_2 by mixed phase FANT-eg nanotubes. The mechanism is arrived at by closely considering pertinent reactions and material properties reported in the literature.[98, 103, 113]

4. Conclusion

Carbon dioxide was photocatalytically transformed into light hydrocarbons using flame annealed TiO_2 nanotubes with methane as the dominant hydrocarbon product and ethane and ethylene as minor products. The CH_4 yields for CO_2 photoreduction using high temperature flame annealed TiO_2 nanotubes are amongst the highest reported for bare TiO_2 nanotubes, and are either comparable to or exceed CH_4 yields obtained with TiO_2 -based functionalized catalysts and

nanocomposites. Isotope labelling experiments performed using GC-MS and gas phase FTIR provided confirmation that the CH₄ is produced by CO₂ photoreduction, and not due to either adventitious carbon or carbon introduced into the nanotubes during the anodic synthesis or the flame annealing treatment. The flame annealed nanotubes exhibited significant photoactivity for CO₂ reduction under visible light irradiation with a peak response at 450 nm and a photocatalytic activity edge that extended to photon energies as low as 2 eV. The visible light activity was attributed to defect-mediated absorption from localized Ti³⁺ states. Given the composition and band-edges of the TiO₂ nanomaterials employed in this study, the carbene pathway is the most likely reaction mechanism for the sunlight driven transformation of CO₂ into methane. In this work, we also generated experimental support for the carbene pathway through the detection of the presence of CO and the absence of HCHO and HCOOH in the product mixture. Square shaped flame annealed nanotubes were found to interact with light in a slightly different manner from regular nanotubes with circular cross-sections, exhibiting a higher density of electromagnetic hot spots for visible light and stronger absorption of ultraviolet photons. Flame annealing partially transformed anatase phase into the more thermodynamically stable rutile phase in ethylene glycol based TiO₂ nanotubes, which in turn, created a favorable band alignment inside the nanotubes enabling charge carrier separation and promoting photocatalytic activity, which resulted in enhanced CO₂ photoreduction to CH₄.

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Conflicts of Interest

The authors have no conflicts to declare.

References

- [1] S.T. Henriques, K.J. Borowiecki, The drivers of long-run CO₂ emissions in Europe, North America and Japan since 1800, *Energy Policy*, 101 (2017) 537-549.
- [2] S.A. Rackley, Carbon capture and storage, Butterworth-Heinemann, Oxford (U.K.), 2017.
- [3] A.W. Kleij, M. North, A. Urakawa, CO₂ Catalysis, *ChemSusChem*, 10 (2017) 1036-1038.
- [4] N. Hicks, U. Vik, P. Taylor, E. Ladoukakis, J. Park, F. Kolisis, K.S. Jakobsen, Using Prokaryotes for Carbon Capture Storage, *Trends Biotechnol.*, 35 (2017) 22-32.
- [5] M. Halmann, Photoelectrochemical reduction of aqueous carbon dioxide on p-type gallium phosphide in liquid junction solar cells, *Nature*, 275 (1978) 115.
- [6] B. Aurian-Blajeni, M. Halmann, J. Manassen, Photoreduction of carbon dioxide and water into formaldehyde and methanol on semiconductor materials, *Solar Energy*, 25 (1980) 165-170.
- [7] S. Navalón, A. Dhakshinamoorthy, M. Álvaro, H. Garcia, Photocatalytic CO₂ Reduction using Non-Titanium Metal Oxides and Sulfides, *ChemSusChem*, 6 (2013) 562-577.
- [8] (!!! INVALID CITATION !!! 8-10).
- [9] S.U.M. Khan, M. Al-Shahry, W.B. Ingler, Efficient Photochemical Water Splitting by a Chemically Modified n-TiO₂, *Science*, 297 (2002) 2243.
- [10] K. Shankar, M. Paulose, G.K. Mor, O.K. Varghese, C.A. Grimes, A study on the spectral photoresponse and photoelectrochemical properties of flame-annealed titania nanotube-arrays, *J. Phys. D: Appl. Phys.*, 38 (2005) 3543.
- [11] K.S. Raja, M. Misra, V.K. Mahajan, T. Gandhi, P. Pillai, S.K. Mohapatra, Photo-electrochemical hydrogen generation using band-gap modified nanotubular titanium oxide in solar light, *J. Power Sources*, 161 (2006) 1450-1457.
- [12] R. Hahn, A. Ghicov, J. Salonen, V.-P. Lehto, P. Schmuki, Carbon doping of self-organized TiO₂ nanotube layers by thermal acetylene treatment, *Nanotechnology*, 18 (2007) 105604.
- [13] C. Xu, Y.A. Shaban, W.B. Ingler, S.U.M. Khan, Nanotube enhanced photoresponse of carbon modified (CM)-n-TiO₂ for efficient water splitting, *Sol. Energy Mater. Sol. Cells*, 91 (2007) 938-943.
- [14] A.B. Murphy, Does carbon doping of TiO₂ allow water splitting in visible light? Comments on "Nanotube enhanced photoresponse of carbon modified (CM)-n-TiO₂ for efficient water splitting", *Sol. Energy Mater. Sol. Cells*, 92 (2008) 363-367.
- [15] X. Chen, L. Liu, Y.Y. Peter, S.S. Mao, Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals, *Science*, 331 (2011) 746-750.
- [16] G. Wang, H. Wang, Y. Ling, Y. Tang, X. Yang, R.C. Fitzmorris, C. Wang, J.Z. Zhang, Y. Li, Hydrogen-treated TiO₂ nanowire arrays for photoelectrochemical water splitting, *Nano Lett.*, 11 (2011) 3026-3033.
- [17] A. Naldoni, M. Allieta, S. Santangelo, M. Marelli, F. Fabbri, S. Cappelli, C.L. Bianchi, R. Psaro, V. Dal Santo, Effect of nature and location of defects on bandgap narrowing in black TiO₂ nanoparticles, *J. Am. Chem. Soc.*, 134 (2012) 7600-7603.
- [18] W. Zhou, W. Li, J.-Q. Wang, Y. Qu, Y. Yang, Y. Xie, K. Zhang, L. Wang, H. Fu, D. Zhao, Ordered Mesoporous Black TiO₂ as Highly Efficient Hydrogen Evolution Photocatalyst, *J. Am. Chem. Soc.*, 136 (2014) 9280-9283.
- [19] N. Liu, C. Schneider, D. Freitag, M. Hartmann, U. Venkatesan, J. Müller, E. Spiecker, P. Schmuki, Black TiO₂ Nanotubes: Cocatalyst-Free Open-Circuit Hydrogen Generation, *Nano Lett.*, 14 (2014) 3309-3313.
- [20] M. Tian, M. Mahjouri-Samani, G. Eres, R. Sachan, M. Yoon, M.F. Chisholm, K. Wang, A.A. Puzetzy, C.M. Rouleau, D.B. Geohegan, G. Duscher, Structure and Formation Mechanism of Black TiO₂ Nanoparticles, *ACS Nano*, 9 (2015) 10482-10488.
- [21] K. Shankar, J.I. Basham, N.K. Allam, O.K. Varghese, G.K. Mor, X. Feng, M. Paulose, J.A. Seabold, K.-S. Choi, C.A. Grimes, Recent Advances in the Use of TiO₂ Nanotube and Nanowire Arrays for Oxidative Photoelectrochemistry, *J. Phys. Chem. C*, 113 (2009) 6327-6359.

- [22] N.T. Nguyen, M. Altomare, J.E. Yoo, N. Taccardi, P. Schmuki, Noble Metals on Anodic TiO₂ Nanotube Mouths: Thermal Dewetting of Minimal Pt Co-Catalyst Loading Leads to Significantly Enhanced Photocatalytic H₂ Generation, *Adv. Energ. Mater.*, 6 (2016) 1501926.
- [23] A. Mohammadpour, P. Kar, B. D Wiltshire, A. M Askar, K. Shankar, Electron transport, trapping and recombination in anodic TiO₂ nanotube arrays, *Curr. Nanosci.*, 11 (2015) 593-614.
- [24] S. Kurian, H. Seo, H. Jeon, Significant Enhancement in Visible Light Absorption of TiO₂ Nanotube Arrays by Surface Band Gap Tuning, *J. Phys. Chem. C*, 117 (2013) 16811-16819.
- [25] K. Shankar, G.K. Mor, A. Fitzgerald, C.A. Grimes, Cation Effect on the Electrochemical Formation of Very High Aspect Ratio TiO₂ Nanotube Arrays in Formamide–Water Mixtures, *J. Phys. Chem. C*, 111 (2007) 21-26.
- [26] O.K. Varghese, D. Gong, M. Paulose, K.G. Ong, E.C. Dickey, C.A. Grimes, Extreme Changes in the Electrical Resistance of Titania Nanotubes with Hydrogen Exposure, *Adv. Mater.*, 15 (2003) 624-627.
- [27] J. Zou, Q. Zhang, K. Huang, N. Marzari, Ultraviolet Photodetectors Based on Anodic TiO₂ Nanotube Arrays, *J. Phys. Chem. C*, 114 (2010) 10725-10729.
- [28] M.H. Zarifi, A. Mohammadpour, S. Farsinezhad, B.D. Wiltshire, M. Nosrati, A.M. Askar, M. Daneshmand, K. Shankar, Time-Resolved Microwave Photoconductivity (TRMC) Using Planar Microwave Resonators: Application to the Study of Long-Lived Charge Pairs in Photoexcited Titania Nanotube Arrays, *J. Phys. Chem. C*, 119 (2015) 14358-14365.
- [29] H. Cui, W. Zhao, C. Yang, H. Yin, T. Lin, Y. Shan, Y. Xie, H. Gu, F. Huang, Black TiO₂ nanotube arrays for high-efficiency photoelectrochemical water-splitting, *J. Mater. Chem. A*, 2 (2014) 8612-8616.
- [30] G.K. Mor, K. Shankar, M. Paulose, O.K. Varghese, C.A. Grimes, Enhanced Photocleavage of Water Using Titania Nanotube Arrays, *Nano Lett.*, 5 (2005) 191-195.
- [31] W.-N. Wang, W.-J. An, B. Ramalingam, S. Mukherjee, D.M. Niedzwiedzki, S. Gangopadhyay, P. Biswas, Size and Structure Matter: Enhanced CO₂ Photoreduction Efficiency by Size-Resolved Ultrafine Pt Nanoparticles on TiO₂ Single Crystals, *J. Am. Chem. Soc.*, 134 (2012) 11276-11281.
- [32] X. Zhang, F. Han, B. Shi, S. Farsinezhad, G.P. Dechaine, K. Shankar, Photocatalytic conversion of diluted CO₂ into light hydrocarbons using periodically modulated multiwalled nanotube arrays, *Angew. Chem.*, 124 (2012) 12904-12907.
- [33] Ishitani, Osamu, C. Inoue, Y. Suzuki, T. Ibusuki, Photocatalytic reduction of carbon dioxide to methane and acetic acid by an aqueous suspension of metal-deposited TiO₂, *Journal of Photochemistry and Photobiology A: Chemistry*, 72 (1993) 269-271.
- [34] Ş. Neaţu, J.A. Maciá-Agulló, P. Concepción, H. Garcia, Gold–Copper Nanoalloys Supported on TiO₂ as Photocatalysts for CO₂ Reduction by Water, *J. Am. Chem. Soc.*, 136 (2014) 15969-15976.
- [35] S. Farsinezhad, H. Sharma, K. Shankar, Interfacial band alignment for photocatalytic charge separation in TiO₂ nanotube arrays coated with CuPt nanoparticles, *Phys. Chem. Chem. Phys.*, 17 (2015) 29723-29733.
- [36] P. Kar, S. Farsinezhad, N. Mahdi, Y. Zhang, U. Obuekwe, H. Sharma, J. Shen, N. Semagina, K. Shankar, Enhanced CH₄ yield by photocatalytic CO₂ reduction using TiO₂ nanotube arrays grafted with Au, Ru, and ZnPd nanoparticles, *Nano Res.*, 9 (2016) 3478-3493.
- [37] J. Jiao, Y. Wei, Y. Zhao, Z. Zhao, A. Duan, J. Liu, Y. Pang, J. Li, G. Jiang, Y. Wang, AuPd/3DOM-TiO₂ catalysts for photocatalytic reduction of CO₂: High efficient separation of photogenerated charge carriers, *Appl. Catal. B-Environ.*, 209 (2017) 228-239.
- [38] M. Tahir, B. Tahir, N.A.S. Amin, Synergistic effect in plasmonic Au/Ag alloy NPs co-coated TiO₂ NWs toward visible-light enhanced CO₂ photoreduction to fuels, *Appl. Catal. B-Environ.*, 204 (2017) 548-560.
- [39] F. Zhou, H. Li, M. Fournier, D.R. MacFarlane, Electrocatalytic CO₂ Reduction to Formate at Low Overpotentials on Electrodeposited Pd Films: Stabilized Performance by Suppression of CO Formation, *ChemSusChem*, 10 (2017) 1509-1516.

- [40] Z. Zhao, Z. Chen, G. Lu, Computational Discovery of Nickel-Based Catalysts for CO₂ Reduction to Formic Acid, *J. Phys. Chem. C*, 121 (2017) 20865-20870.
- [41] P. Kar, S. Farsinezhad, X. Zhang, K. Shankar, Anodic Cu₂S and CuS nanorod and nanowall arrays: preparation, properties and application in CO₂ photoreduction, *Nanoscale*, 6 (2014) 14305-14318.
- [42] S. Thomas, K. Stefanie, P. Kristin, P. Oliver, D. Kay, F. Daniel, O. Ivan, S. Adriana, K. Ernst-Bernhard, T. Andreas, Materials Pushing the Application Limits of Wire Grid Polarizers further into the Deep Ultraviolet Spectral Range, *Advanced Optical Materials*, 4 (2016) 1780-1786.
- [43] Y. Zhang, S. Farsinezhad, B.D. Wiltshire, R. Kisslinger, P. Kar, K. Shankar, Optical anisotropy in vertically oriented TiO₂ nanotube arrays, *Nanotechnology*, 28 (2017) 374001.
- [44] K. Shankar, G.K. Mor, H.E. Prakasam, S. Yoriya, M. Paulose, O.K. Varghese, C.A. Grimes, Highly-ordered TiO₂ nanotube arrays up to 220 μm in length: use in water photoelectrolysis and dye-sensitized solar cells, *Nanotechnology*, 18 (2007) 065707.
- [45] S. Farsinezhad, P.R. Waghmare, B.D. Wiltshire, H. Sharma, S. Amiri, S.K. Mitra, K. Shankar, Amphiphobic surfaces from functionalized TiO₂ nanotube arrays, *RSC Adv.*, 4 (2014) 33587-33598.
- [46] M.A. Khan, H.-T. Jung, O.-B. Yang, Synthesis and characterization of ultrahigh crystalline TiO₂ nanotubes, *J. Phys. Chem. B*, 110 (2006) 6626-6630.
- [47] M.-J. López-Muñoz, A. Arencibia, L. Cerro, R. Pascual, Á. Melgar, Adsorption of Hg (II) from aqueous solutions using TiO₂ and titanate nanotube adsorbents, *Appl. Surf. Sci.*, 367 (2016) 91-100.
- [48] Y. Sun, K. Yan, G. Wang, W. Guo, T. Ma, Effect of annealing temperature on the hydrogen production of TiO₂ nanotube arrays in a two-compartment photoelectrochemical cell, *J. Phys. Chem. C*, 115 (2011) 12844-12849.
- [49] M. Jarosz, K. Syrek, J. Kapusta-Kołodziej, J. Mech, K. Małek, K. Hnida, T. Łojewski, M. Jaskuła, G.D. Sulka, Heat Treatment Effect on Crystalline Structure and Photoelectrochemical Properties of Anodic TiO₂ Nanotube Arrays Formed in Ethylene Glycol and Glycerol Based Electrolytes, *J. Phys. Chem. C*, 119 (2015) 24182-24191.
- [50] W. Li, C. Ni, H. Lin, C. Huang, S.I. Shah, Size dependence of thermal stability of TiO₂ nanoparticles, *J. Appl. Phys.*, 96 (2004) 6663-6668.
- [51] H. Nakajima, T. Mori, Q. Shen, T. Toyoda, Photoluminescence study of mixtures of anatase and rutile TiO₂ nanoparticles: influence of charge transfer between the nanoparticles on their photoluminescence excitation bands, *Chem. Phys. Lett.*, 409 (2005) 81-84.
- [52] R. Su, R. Bechstein, L. Sjø, R.T. Vang, M. Sillassen, B. Esbjornsson, A. Palmqvist, F. Besenbacher, How the anatase-to-rutile ratio influences the photoreactivity of TiO₂, *J. Phys. Chem. C*, 115 (2011) 24287-24292.
- [53] W. Su, J. Zhang, Z. Feng, T. Chen, P. Ying, C. Li, Surface phases of TiO₂ nanoparticles studied by UV Raman spectroscopy and FT-IR spectroscopy, *J. Phys. Chem. C*, 112 (2008) 7710-7716.
- [54] J.-G. Li, T. Ishigaki, X. Sun, Anatase, brookite, and rutile nanocrystals via redox reactions under mild hydrothermal conditions: phase-selective synthesis and physicochemical properties, *J. Phys. Chem. C*, 111 (2007) 4969-4976.
- [55] A.S. Attar, Z. Hassani, Fabrication and growth mechanism of single-crystalline rutile TiO₂ nanowires by liquid-phase deposition process in a porous alumina template, *J. Mater. Sci. Technol.*, 31 (2015) 828-833.
- [56] B. Di Bartolo, Optical interactions in solids, World Scientific Publishing Company 2010.
- [57] Z. Pei, L. Ding, H. Lin, S. Weng, Z. Zheng, Y. Hou, P. Liu, Facile synthesis of defect-mediated TiO_{2-x} with enhanced visible light photocatalytic activity, *J. Mater. Chem. A*, 1 (2013) 10099-10102.
- [58] F. Zuo, L. Wang, T. Wu, Z. Zhang, D. Borchardt, P. Feng, Self-doped Ti³⁺ enhanced photocatalyst for hydrogen production under visible light, *J. Am. Chem. Soc.*, 132 (2010) 11856-11857.
- [59] C. Di Valentin, A. Selloni, Bulk and surface polarons in photoexcited anatase TiO₂, *The Journal of Physical Chemistry Letters*, 2 (2011) 2223-2228.

- [60] P. Johnson, R. Christy, Optical constants of transition metals: Ti, V, Cr, Mn, Fe, Co, Ni, and Pd, *Phys. Rev. B*, 9 (1974) 5056.
- [61] T. Berger, J.A. Anta, V.c. Morales-Flórez, Electrons in the band gap: spectroscopic characterization of anatase TiO₂ nanocrystal electrodes under Fermi level control, *J. Phys. Chem. C*, 116 (2012) 11444-11455.
- [62] Z. Wang, B. Wen, Q. Hao, L.-M. Liu, C. Zhou, X. Mao, X. Lang, W.-J. Yin, D. Dai, A. Selloni, X. Yang, Localized Excitation of Ti³⁺ Ions in the Photoabsorption and Photocatalytic Activity of Reduced Rutile TiO₂, *J. Am. Chem. Soc.*, 137 (2015) 9146-9152.
- [63] M. Paulose, K. Shankar, S. Yoriya, H.E. Prakasam, O.K. Varghese, G.K. Mor, T.A. Latempa, A. Fitzgerald, C.A. Grimes, Anodic growth of highly ordered TiO₂ nanotube arrays to 134 μm in length, *J. Phys. Chem. B*, 110 (2006) 16179-16184.
- [64] C. Di Valentin, G. Pacchioni, A. Selloni, Reduced and n-type doped TiO₂: nature of Ti³⁺ species, *J. Phys. Chem. C*, 113 (2009) 20543-20552.
- [65] M. Rajabi, S. Shogh, Defect study of TiO₂ nanorods grown by a hydrothermal method through photoluminescence spectroscopy, *J. Lumin.*, 157 (2015) 235-242.
- [66] Y. Chen, W. Li, J. Wang, Y. Gan, L. Liu, M. Ju, Microwave-assisted ionic liquid synthesis of Ti³⁺ self-doped TiO₂ hollow nanocrystals with enhanced visible-light photoactivity, *Appl. Catal. B-Environ.*, 191 (2016) 94-105.
- [67] Y. Zhou, C. Chen, N. Wang, Y. Li, H. Ding, Stable Ti³⁺ Self-Doped Anatase-Rutile Mixed TiO₂ with Enhanced Visible Light Utilization and Durability, *J. Phys. Chem. C*, 120 (2016) 6116-6124.
- [68] J. Chen, W. Song, H. Hou, Y. Zhang, M. Jing, X. Jia, X. Ji, Ti³⁺ Self-Doped Dark Rutile TiO₂ Ultrafine Nanorods with Durable High-Rate Capability for Lithium-Ion Batteries, *Adv. Funct. Mater.*, 25 (2015) 6793-6801.
- [69] Y. Yang, P. Gao, X. Ren, L. Sha, P. Yang, J. Zhang, Y. Chen, L. Yang, Massive Ti³⁺ self-doped by the injected electrons from external Pt and the efficient photocatalytic hydrogen production under visible-light, *Appl. Catal. B-Environ.*, 218 (2017) 751-757.
- [70] L. Liu, Y. Jiang, H. Zhao, J. Chen, J. Cheng, K. Yang, Y. Li, Engineering Coexposed {001} and {101} Facets in Oxygen-Deficient TiO₂ Nanocrystals for Enhanced CO₂ Photoreduction under Visible Light, *ACS Catal.*, 6 (2016) 1097-1108.
- [71] C. Mao, F. Zuo, Y. Hou, X. Bu, P. Feng, In Situ Preparation of a Ti³⁺ Self-Doped TiO₂ Film with Enhanced Activity as Photoanode by N₂H₄ Reduction, *Angew. Chem., Int. Ed.*, 53 (2014) 10485-10489.
- [72] Z. Lian, W. Wang, G. Li, F. Tian, K.S. Schanze, H. Li, Pt-Enhanced Mesoporous Ti³⁺/TiO₂ with Rapid Bulk to Surface Electron Transfer for Photocatalytic Hydrogen Evolution, *ACS Appl. Mater. Inter.*, 9 (2017) 16959-16966.
- [73] R. Kumar, S. Govindarajan, R.K. Siri Kiran Janardhana, T.N. Rao, S.V. Joshi, S. Anandan, Facile One-Step Route for the Development of in Situ Cocatalyst-Modified Ti³⁺ Self-Doped TiO₂ for Improved Visible-Light Photocatalytic Activity, *ACS Appl. Mater. Inter.*, 8 (2016) 27642-27653.
- [74] B. Jiang, Y. Tang, Y. Qu, J.-Q. Wang, Y. Xie, C. Tian, W. Zhou, H. Fu, Thin carbon layer coated Ti³⁺-TiO₂ nanocrystallites for visible-light driven photocatalysis, *Nanoscale*, 7 (2015) 5035-5045.
- [75] S. Hoang, S.P. Berglund, N.T. Hahn, A.J. Bard, C.B. Mullins, Enhancing visible light photo-oxidation of water with TiO₂ nanowire arrays via cotreatment with H₂ and NH₃: synergistic effects between Ti³⁺ and N, *J. Am. Chem. Soc.*, 134 (2012) 3659-3662.
- [76] C. Mao, F. Zuo, Y. Hou, X. Bu, P. Feng, In situ preparation of a Ti³⁺ self-doped TiO₂ film with enhanced activity as photoanode by N₂H₄ reduction, *Angew. Chem.*, 126 (2014) 10653-10657.
- [77] R.F. Howe, M. Gratzel, EPR observation of trapped electrons in colloidal titanium dioxide, *The Journal of Physical Chemistry*, 89 (1985) 4495-4499.

- [78] L.R. Grabstanowicz, S. Gao, T. Li, R.M. Rickard, T. Rajh, D.-J. Liu, T. Xu, Facile oxidative conversion of TiH₂ to high-concentration Ti³⁺-self-doped rutile TiO₂ with visible-light photoactivity, *Inorg. Chem.*, 52 (2013) 3884-3890.
- [79] M. Nishikawa, Y. Mitani, Y. Nosaka, Photocatalytic Reaction Mechanism of Fe(III)-Grafted TiO₂ Studied by Means of ESR Spectroscopy and Chemiluminescence Photometry, *J. Phys. Chem. C*, 116 (2012) 14900-14907.
- [80] C.-C. Chen, S.-H. Hu, Y.-P. Fu, Effects of surface hydroxyl group density on the photocatalytic activity of Fe³⁺-doped TiO₂, *J. Alloys Compd.*, 632 (2015) 326-334.
- [81] B. Fang, A. Bonakdarpour, K. Reilly, Y. Xing, F. Taghipour, D.P. Wilkinson, Large-scale synthesis of TiO₂ microspheres with hierarchical nanostructure for highly efficient photodriven reduction of CO₂ to CH₄, *ACS Appl. Mater. Inter.*, 6 (2014) 15488-15498.
- [82] Q. Zhai, S. Xie, W. Fan, Q. Zhang, Y. Wang, W. Deng, Y. Wang, Photocatalytic conversion of carbon dioxide with water into methane: platinum and copper (I) oxide co-catalysts with a core-shell structure, *Angew. Chem.*, 125 (2013) 5888-5891.
- [83] T. Yui, A. Kan, C. Saitoh, K. Koike, T. Ibusuki, O. Ishitani, Photochemical reduction of CO₂ using TiO₂: effects of organic adsorbates on TiO₂ and deposition of Pd onto TiO₂, *ACS Appl. Mater. Inter.*, 3 (2011) 2594-2600.
- [84] B. Fang, Y. Xing, A. Bonakdarpour, S. Zhang, D.P. Wilkinson, Hierarchical CuO-TiO₂ hollow microspheres for highly efficient photodriven reduction of CO₂ to CH₄, *ACS Sustain. Chem. Eng.*, 3 (2015) 2381-2388.
- [85] M. Anpo, M. Takeuchi, The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation, *J. Catal.*, 216 (2003) 505-516.
- [86] D. Luo, W. Ma, L. Wu, K. Nakata, CO₂ Reduction by Photocatalysis on TiO₂, *Advanced Solid Catalysts for Renewable Energy Production*, IGI Global 2018, pp. 268-299.
- [87] G. Liu, N. Hoivik, K. Wang, H. Jakobsen, Engineering TiO₂ nanomaterials for CO₂ conversion/solar fuels, *Sol. Energy Mater. Sol. Cells*, 105 (2012) 53-68.
- [88] Z. Xiong, Y. Luo, Y. Zhao, J. Zhang, C. Zheng, J.C. Wu, Synthesis, characterization and enhanced photocatalytic CO₂ reduction activity of graphene supported TiO₂ nanocrystals with coexposed {001} and {101} facets, *Phys. Chem. Chem. Phys.*, 18 (2016) 13186-13195.
- [89] A. Dhakshinamoorthy, S. Navalon, A. Corma, H. Garcia, Photocatalytic CO₂ reduction by TiO₂ and related titanium containing solids, *Energ. Environ. Sci.*, 5 (2012) 9217-9233.
- [90] S.t. Neațu, J.A. Maciá-Agulló, P. Concepción, H. Garcia, Gold-copper nanoalloys supported on TiO₂ as photocatalysts for CO₂ reduction by water, *J. Am. Chem. Soc.*, 136 (2014) 15969-15976.
- [91] J. Yu, J. Low, W. Xiao, P. Zhou, M. Jaroniec, Enhanced photocatalytic CO₂-reduction activity of anatase TiO₂ by coexposed {001} and {101} facets, *J. Am. Chem. Soc.*, 136 (2014) 8839-8842.
- [92] D. Scarano, S. Bertarione, G. Spoto, A. Zecchina, C.O. Arean, FTIR spectroscopy of hydrogen, carbon monoxide, and methane adsorbed and co-adsorbed on zinc oxide, *Thin Solid Films*, 400 (2001) 50-55.
- [93] R.S. McDowell, The ν₃ infrared bands of C₁₂H₄ and C₁₃H₄, *J. Mol. Spectrosc.*, 21 (1966) 280-290.
- [94] S.W. Reeve, W.A. Burns, Rotational Analysis of FTIR Spectra from Cigarette Smoke, *J. Chem. Educ.*, 81 (2004) 865-867.
- [95] X.-H. Xia, Z.-J. Jia, Y. Yu, Y. Liang, Z. Wang, L.-L. Ma, Preparation of multi-walled carbon nanotube supported TiO₂ and its photocatalytic activity in the reduction of CO₂ with H₂O, *Carbon*, 45 (2007) 717-721.
- [96] K. Kočí, L. Obalová, L. Matějová, D. Plachá, Z. Lacný, J. Jirkovský, O. Šolcová, Effect of TiO₂ particle size on the photocatalytic reduction of CO₂, *Appl. Catal. B-Environ.*, 89 (2009) 494-502.
- [97] E.V. Kondratenko, G. Mul, J. Baltrusaitis, G.O. Larrazábal, J. Pérez-Ramírez, Status and perspectives of CO₂ conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes, *Energ. Environ. Sci.*, 6 (2013) 3112-3135.

- [98] S.N. Habisreutinger, L. Schmidt-Mende, J.K. Stolarczyk, Photocatalytic reduction of CO₂ on TiO₂ and other semiconductors, *Angew. Chem., Int. Ed.*, 52 (2013) 7372-7408.
- [99] M. Li, W. Hebenstreit, U. Diebold, A.M. Tyryshkin, M.K. Bowman, G.G. Dunham, M.A. Henderson, The influence of the bulk reduction state on the surface structure and morphology of rutile TiO₂ (110) single crystals, *J. Phys. Chem. B*, 104 (2000) 4944-4950.
- [100] W.-J. Yin, M. Krack, B. Wen, S.-Y. Ma, L.-M. Liu, CO₂ capture and conversion on rutile TiO₂ (110) in the water environment: insight by first-principles calculations, *The journal of physical chemistry letters*, 6 (2015) 2538-2545.
- [101] R.I. Bickley, T. Gonzalez-Carreno, J.S. Lees, L. Palmisano, R.J. Tilley, A structural investigation of titanium dioxide photocatalysts, *J. Solid State Chem.*, 92 (1991) 178-190.
- [102] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh, M.C. Thurnauer, Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase TiO₂ using EPR, *J. Phys. Chem. B*, 107 (2003) 4545-4549.
- [103] D.O. Scanlon, C.W. Dunnill, J. Buckeridge, S.A. Shevlin, A.J. Logsdail, S.M. Woodley, C.R.A. Catlow, M.J. Powell, R.G. Palgrave, I.P. Parkin, Band alignment of rutile and anatase TiO₂, *Nat. Mater.*, 12 (2013) 798.
- [104] S. Leytner, J.T. Hupp, Evaluation of the energetics of electron trap states at the nanocrystalline titanium dioxide/aqueous solution interface via time-resolved photoacoustic spectroscopy, *Chem. Phys. Lett.*, 330 (2000) 231-236.
- [105] Ş. Neaţu, J.A. Maciá-Agulló, H. Garcia, Solar light photocatalytic CO₂ reduction: general considerations and selected bench-mark photocatalysts, *International journal of molecular sciences*, 15 (2014) 5246-5262.
- [106] F. Amano, M. Nakata, A. Yamamoto, T. Tanaka, Effect of Ti³⁺ Ions and Conduction Band Electrons on Photocatalytic and Photoelectrochemical Activity of Rutile Titania for Water Oxidation, *J. Phys. Chem. C*, 120 (2016) 6467-6474.
- [107] L. Liu, Y. Li, Understanding the reaction mechanism of photocatalytic reduction of CO₂ with H₂O on TiO₂-based photocatalysts: a review, *Aerosol Air Qual Res*, 14 (2014) 453-469.
- [108] K.J. Rajalakshmi, V. Krishnamurthy, K R; Viswanathan, B, Photocatalytic reduction of carbon dioxide by water on titania: Role of photophysical and structural properties, *Indian Journal of Chemistry*, 51A (2012) 411-419.
- [109] M. Anpo, H. Yamashita, Y. Ichihashi, S. Ehara, Photocatalytic reduction of CO₂ with H₂O on various titanium oxide catalysts, *J. Electroanal. Chem.*, 396 (1995) 21-26.
- [110] C.-C. Yang, Y.-H. Yu, B. van der Linden, J.C. Wu, G. Mul, Artificial photosynthesis over crystalline TiO₂-based catalysts: fact or fiction?, *J. Am. Chem. Soc.*, 132 (2010) 8398-8406.
- [111] N.M. Dimitrijevic, B.K. Vijayan, O.G. Poluektov, T. Rajh, K.A. Gray, H. He, P. Zapol, Role of water and carbonates in photocatalytic transformation of CO₂ to CH₄ on titania, *J. Am. Chem. Soc.*, 133 (2011) 3964-3971.
- [112] L. Liu, H. Zhao, J.M. Andino, Y. Li, Photocatalytic CO₂ reduction with H₂O on TiO₂ nanocrystals: Comparison of anatase, rutile, and brookite polymorphs and exploration of surface chemistry, *ACS Catal.*, 2 (2012) 1817-1828.
- [113] W.-K. Wang, J.-J. Chen, X. Zhang, Y.-X. Huang, W.-W. Li, H.-Q. Yu, Self-induced synthesis of phase-junction TiO₂ with a tailored rutile to anatase ratio below phase transition temperature, *Sci. Rep.-UK*, 6 (2016) 20491.

SUPPLEMENTARY INFORMATION

High Rate CO₂ Photoreduction Using Flame Annealed TiO₂ Nanotubes

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Conversion of CH₄ peak area to moles of CH₄

Given that air contains 1.85 ppm of CH₄, we calibrated the GC FID with air for quantification of CH₄. Therefore, parts per million of (ppm_{CH_4}) in our sample gas was calculated using eq. (s1).

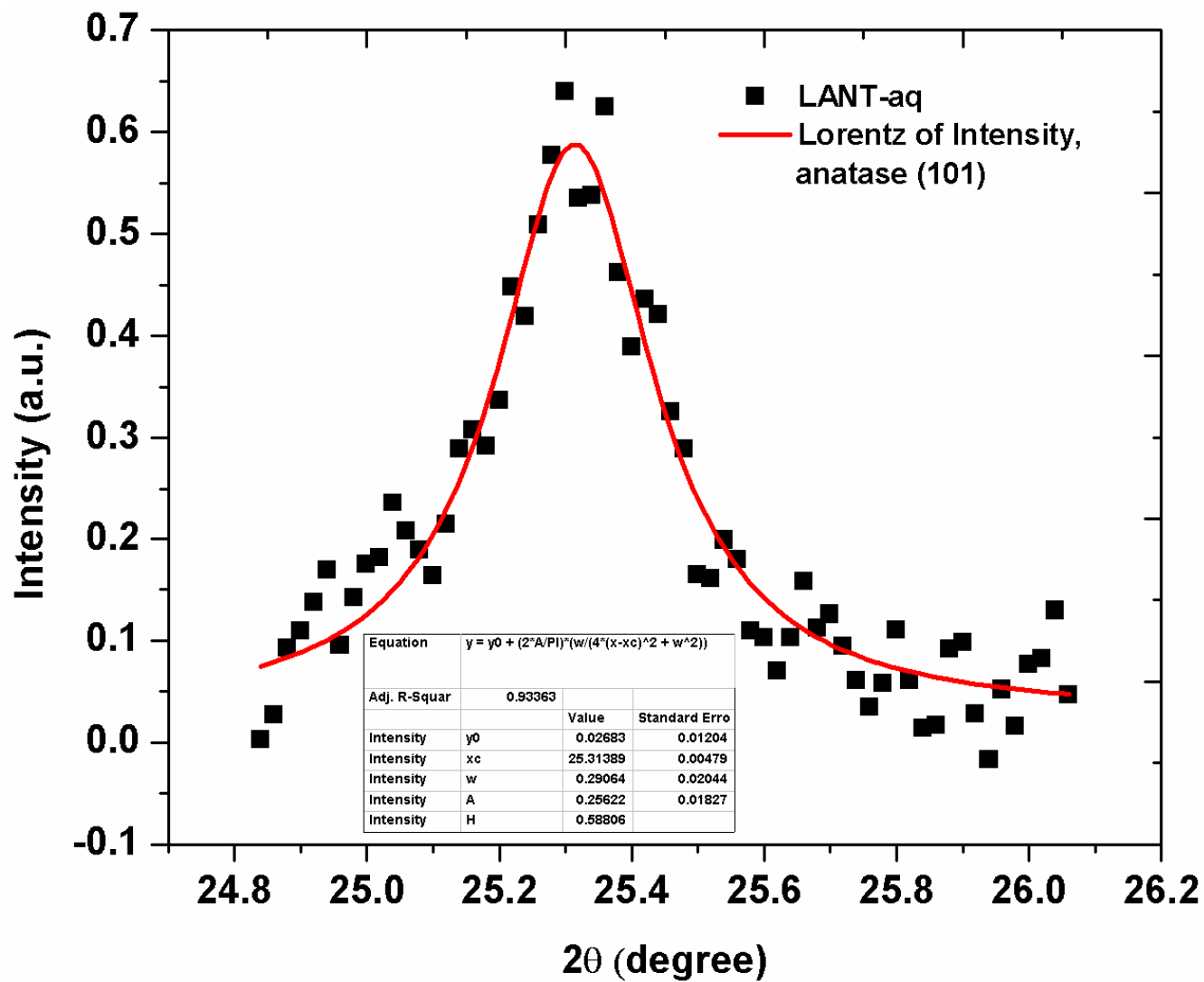
$$ppm_{CH_4} = \frac{\text{Peak area of CH}_4 \text{ in sample}}{\text{Peak area of CH}_4 \text{ in air}} \times 1.85 \quad \text{eq. (s1)}$$

$$M_{CH_4} = \frac{ppm_{CH_4}}{1000000} \quad \text{eq. (s2)}$$

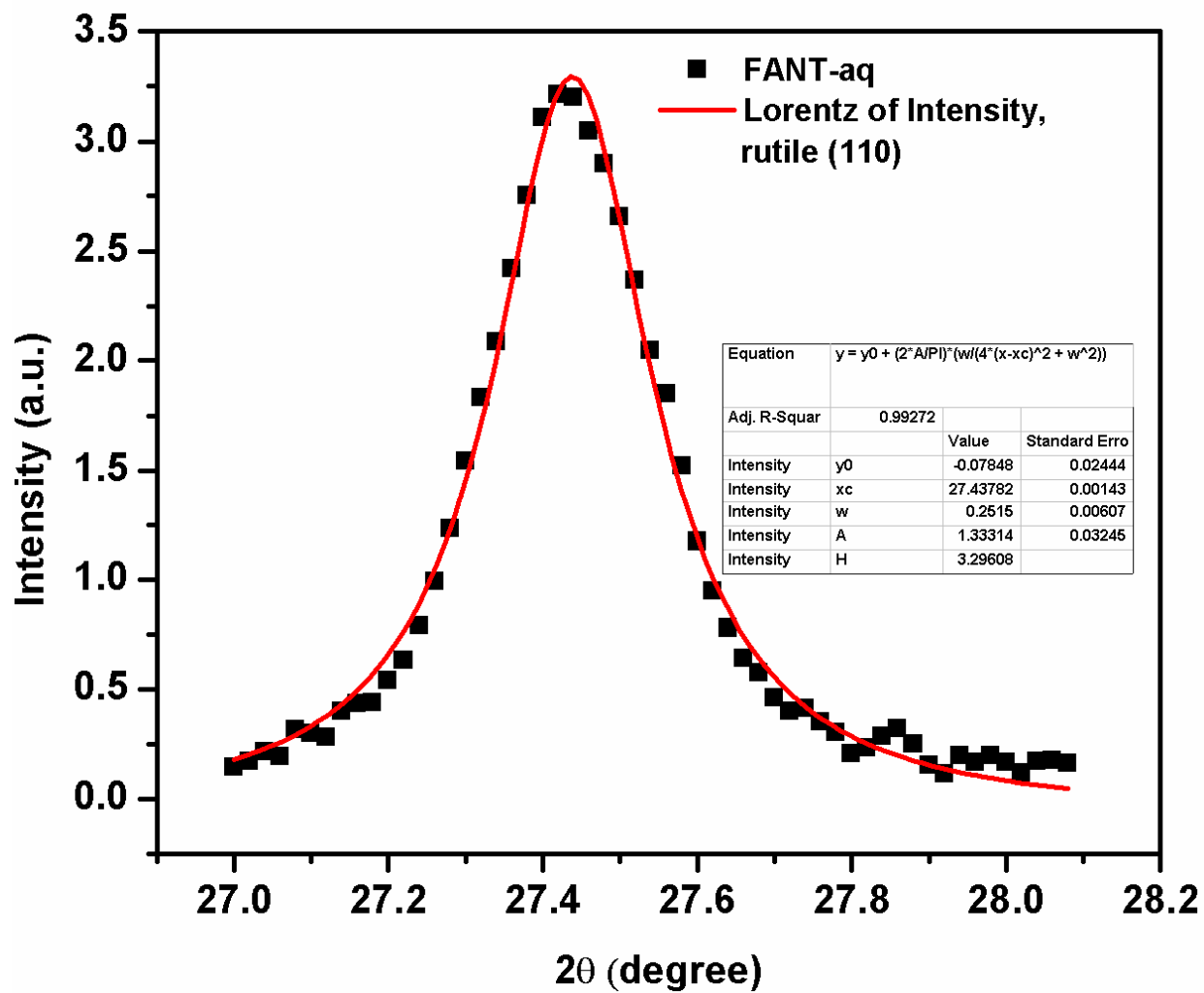
M_{CH_4} is the mole fraction of methane in the reactor and it is calculated using eq. (s2). M_{CH_4} is the ppm value of CH₄ (i.e. ppm_{CH_4}) divided by 1000000. By applying Dalton's law of partial pressure for mole fraction of gas, we obtain (using eq. (s3)) the partial pressure of CH₄ in the reactor by using the total pressure (50 psi) inside the reactor. The number of moles of CH₄ was calculated using gas law (i.e. eq. (s4)), where V is the volume of the reactor (i.e. 30 mL), T is the temperature (i.e. 298 K) and R is the Universal Gas constant (i.e. 8.314 J/m-K). The total number of moles of CH₄ generated was calculated using eq (s4).

$$P_{CH_4} = 50 \times M_{CH_4} \quad \text{eq. (s3)}$$

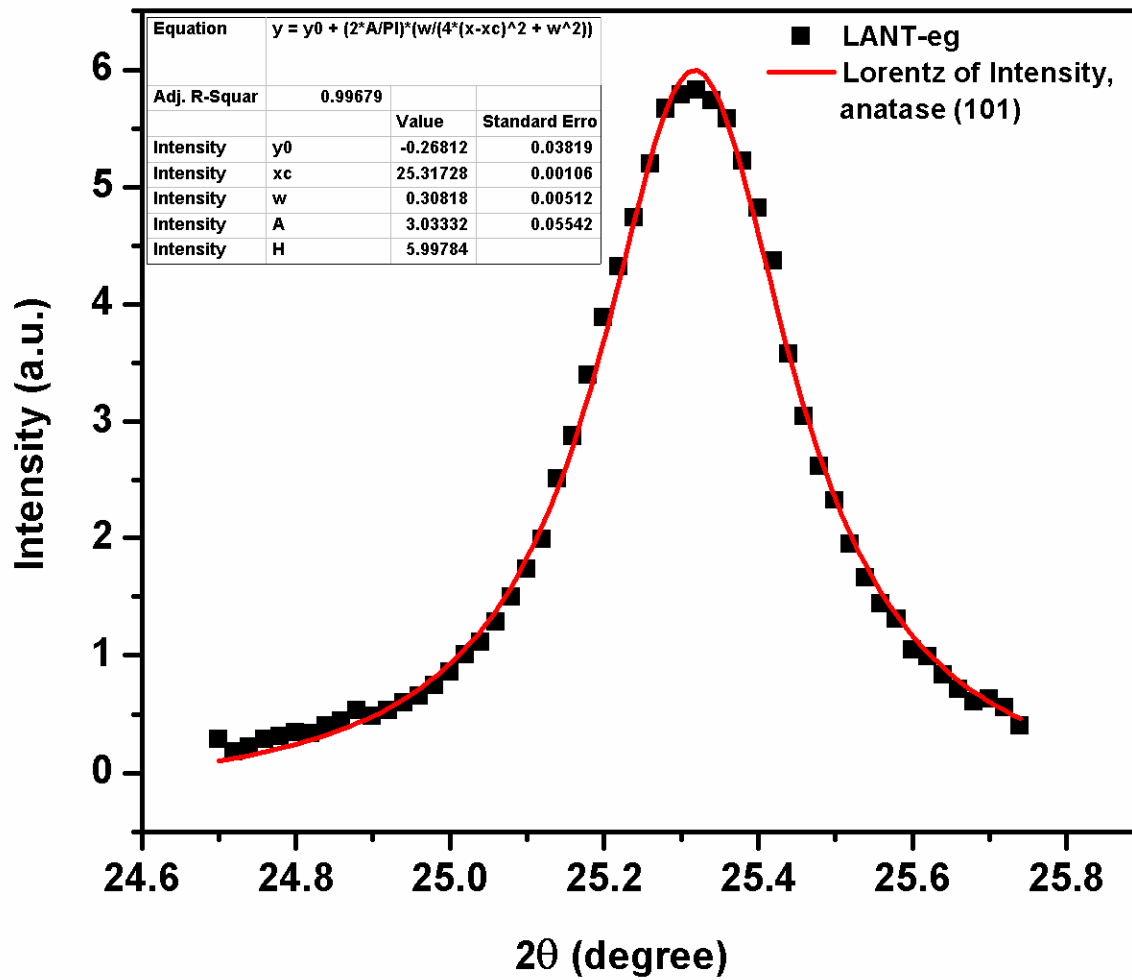
$$n_{CH_4} = \frac{P_{CH_4} V}{RT} \quad \text{eq. (s4)}$$



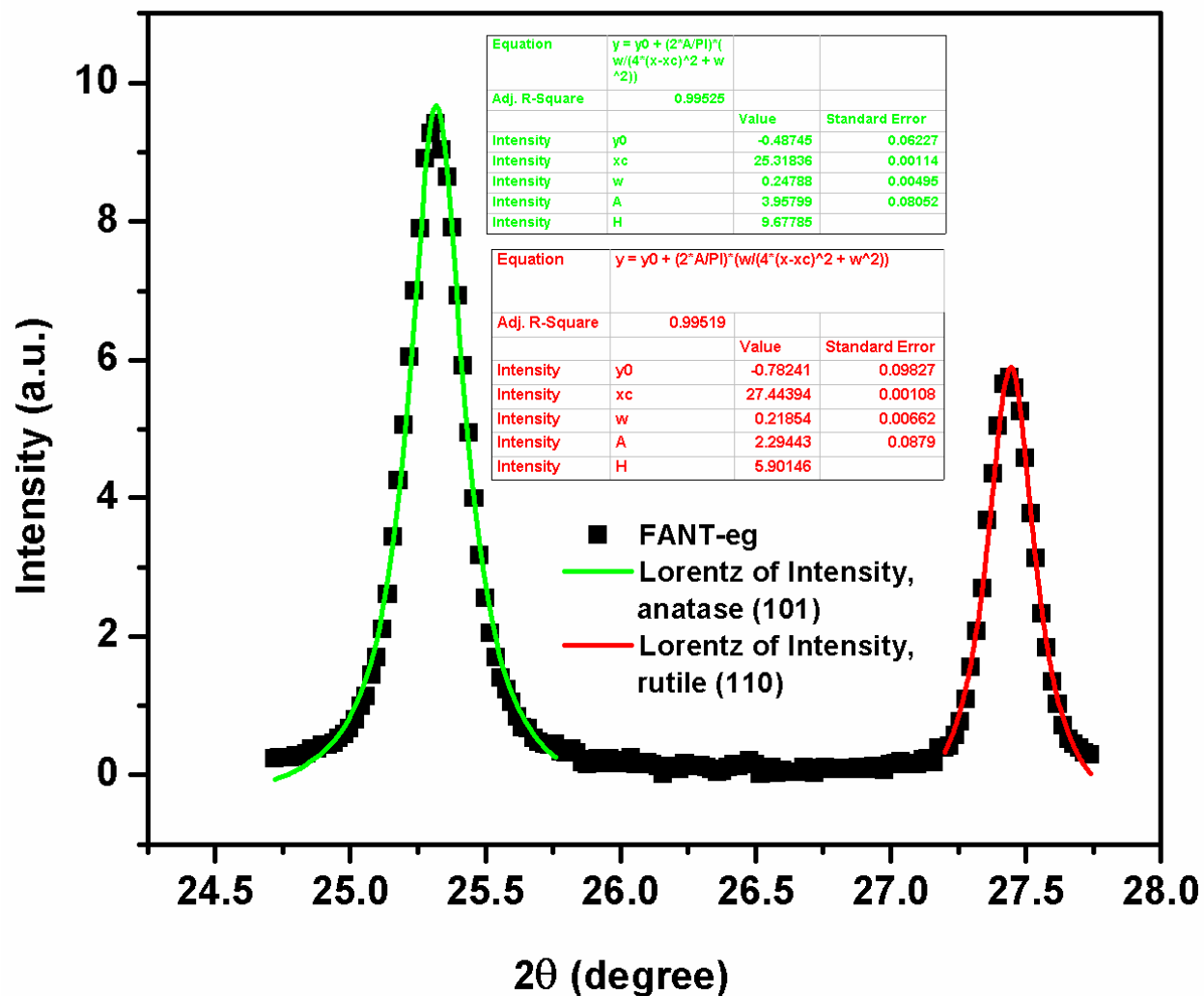
S1a



S1b

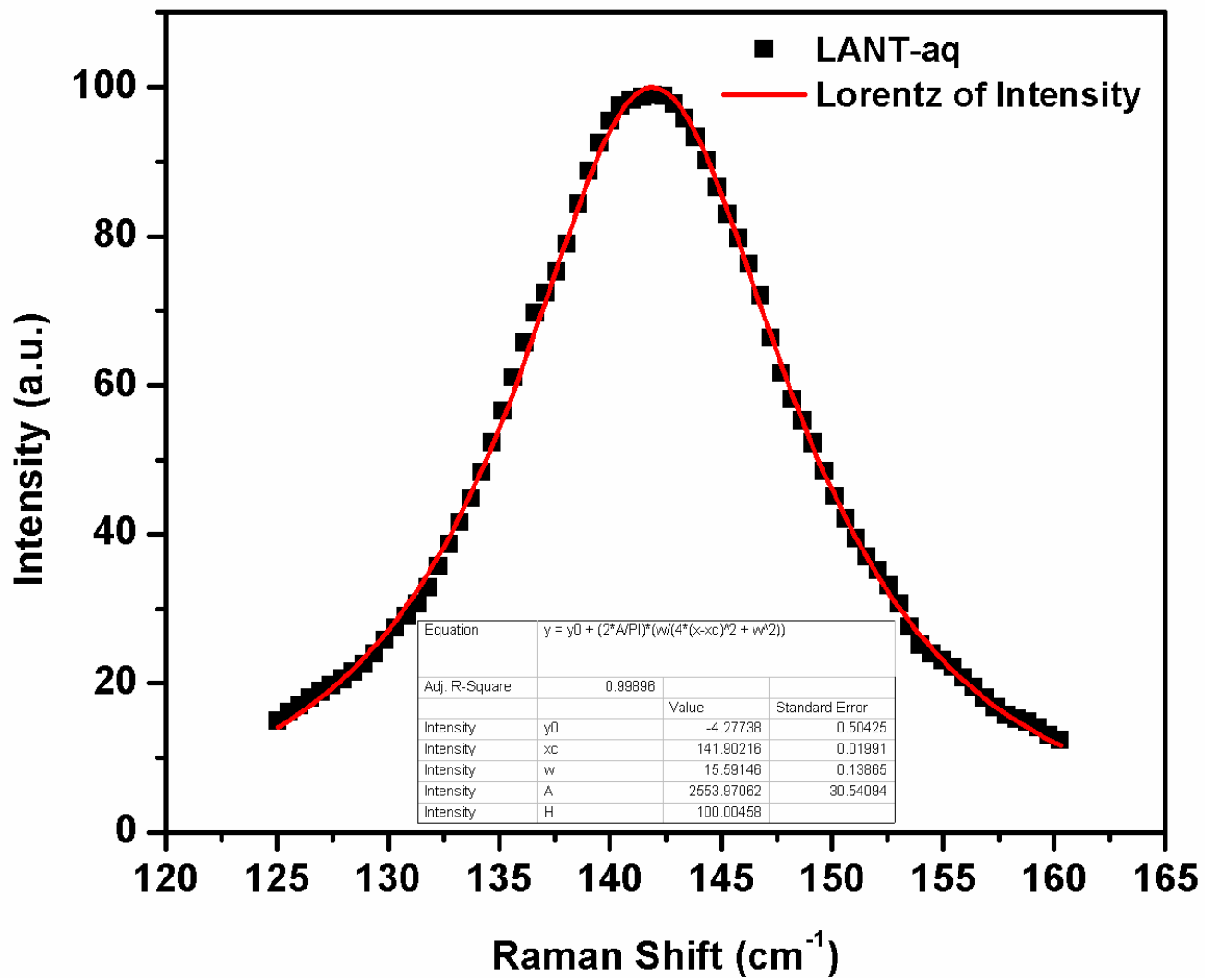


S1c

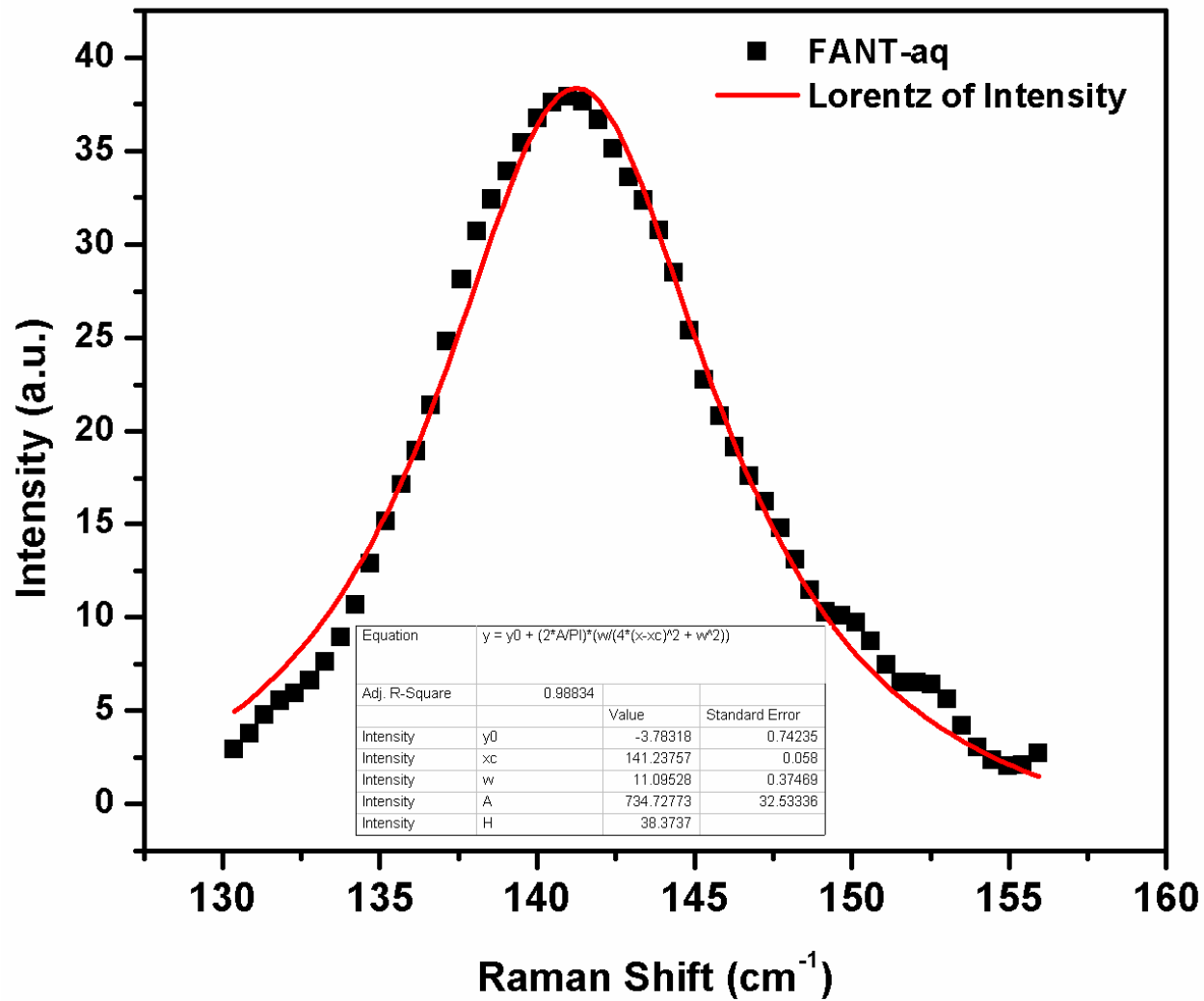


S1d

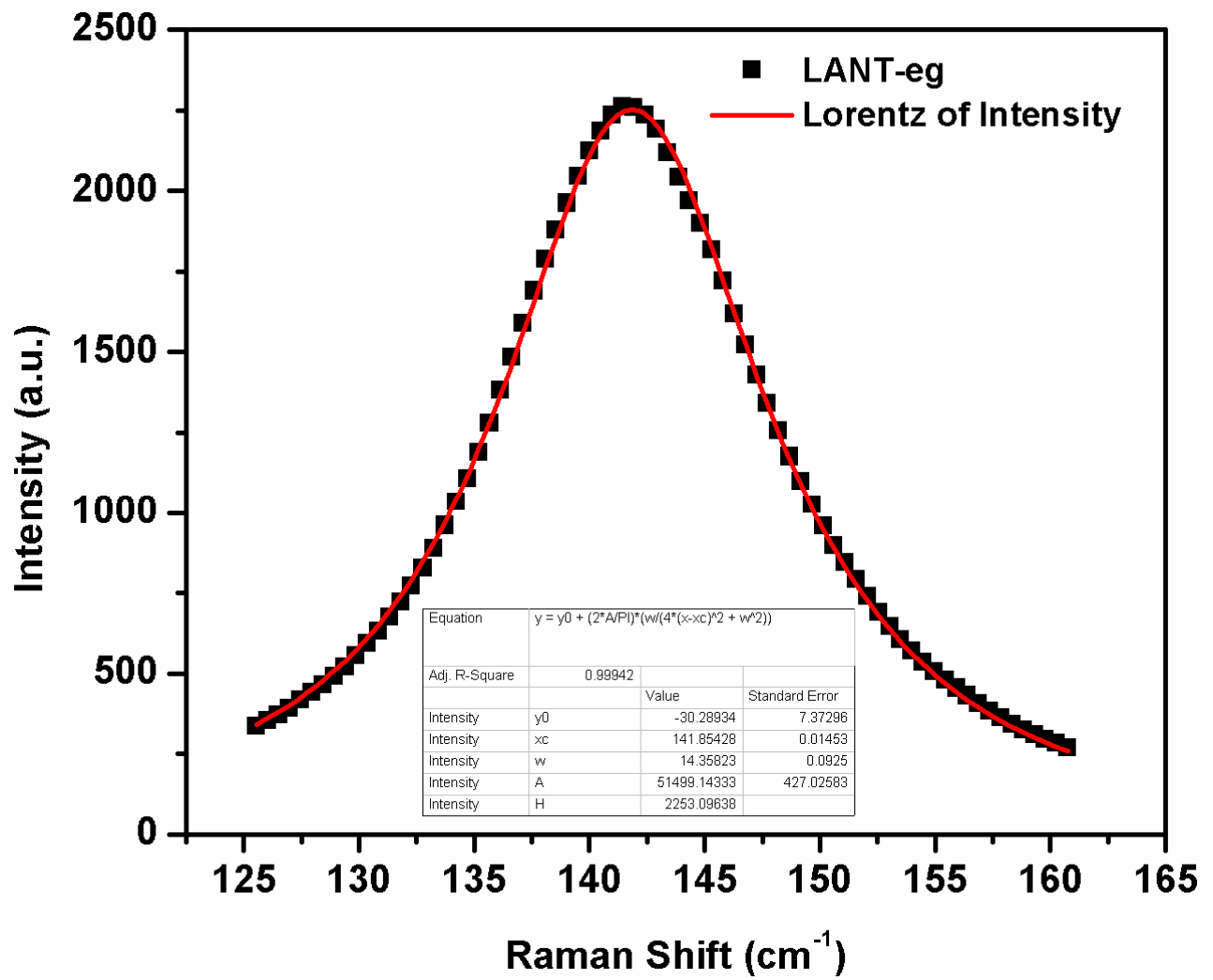
Figure S1. (a) Lorentz fits of anatase (101) and rutile (110) XRD peaks, from which the peak widths at half of maximum intensities were obtained. Here: (a), (b), (c) and (d) are for LANT-aq, FANT-aq, LANT-eg and FANT-eg, respectively.



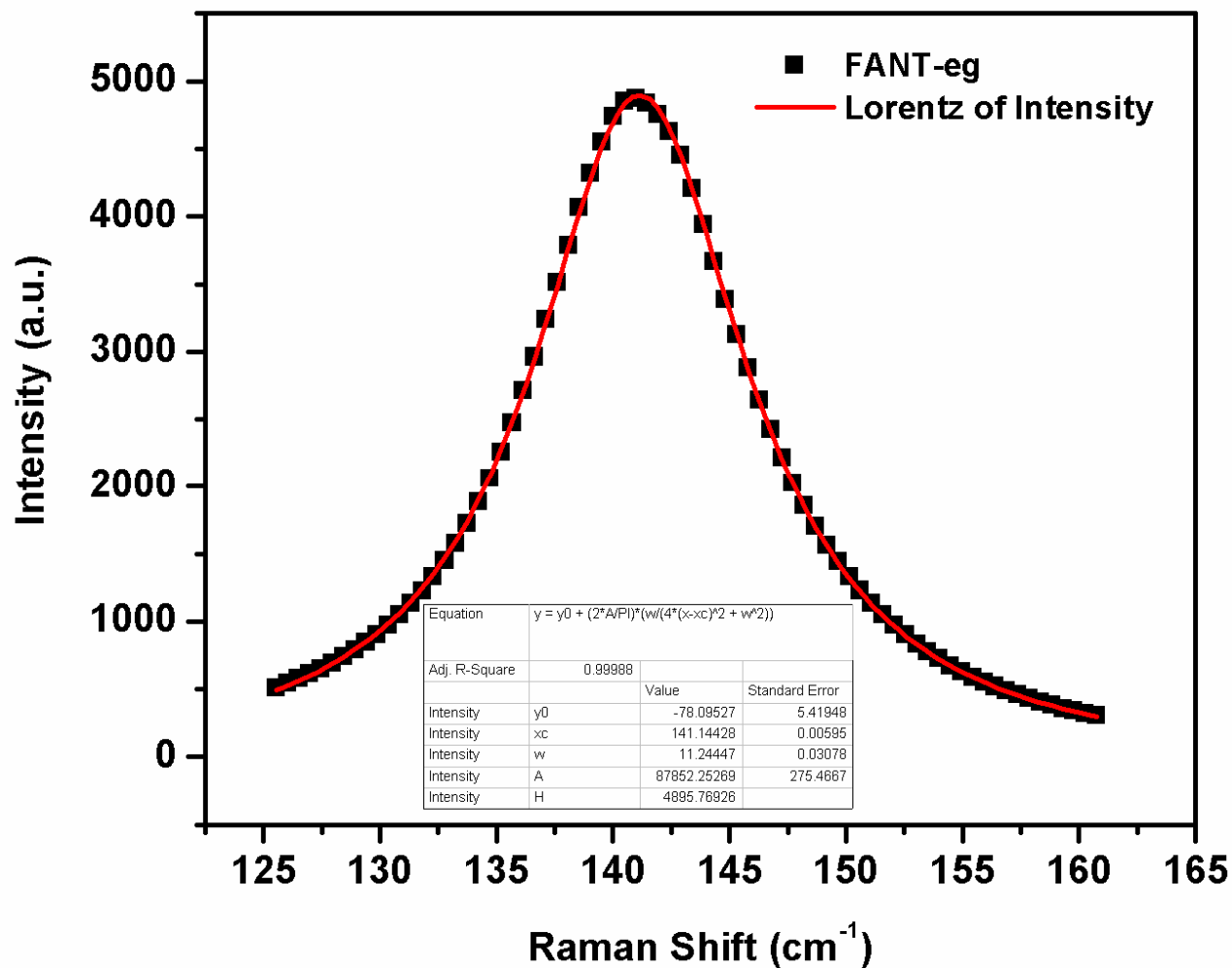
S2a



S2b



S2c



S2d

Figure S2. (a) Lorentz fits of Eg Raman mode of the nanotubes, from which the peak widths at half of maximum intensities were obtained. Here: (a), (b), (c) and (d) are for LANT-aq, FANT-aq, LANT-eg and FANT-eg, respectively.

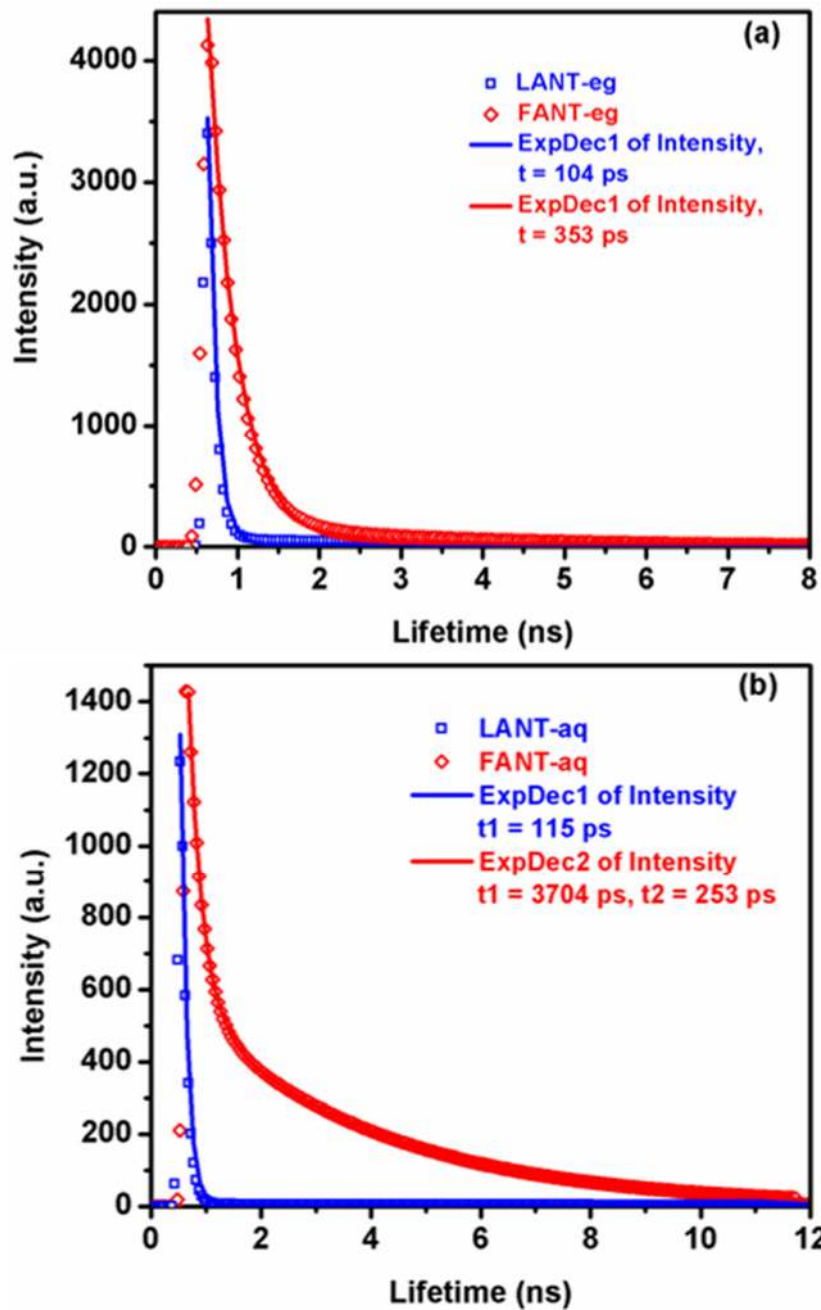


Figure S3. Fluorescence lifetime imaging lifetime decay plots FLIM decay plots showing fluorescence lifetime distributions for the different nanotube types. Flame annealed TiO₂ nanotubes (FANT-eg and FANT-aq) have longer lifetimes than regular nanotubes (LANT-eg and LANT-aq).

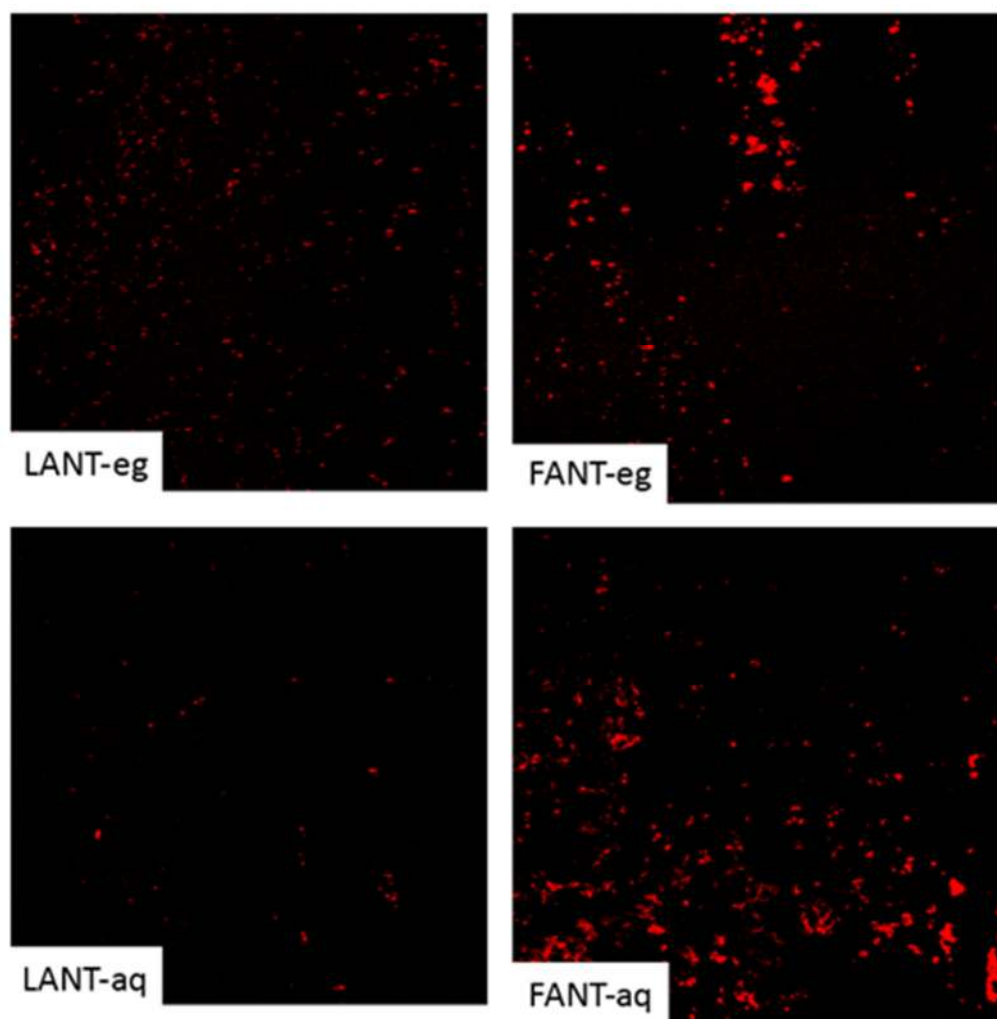


Figure S4. 2-photon fluorescence images of the nanotubes at excitation wavelength of 750 nm. Emission was between 394 and 750 nm. Flame annealed TiO₂ nanotubes (FANT-eg and FANT-aq) have a brighter emission than regular nanotubes (LANT-eg and LANT-aq).

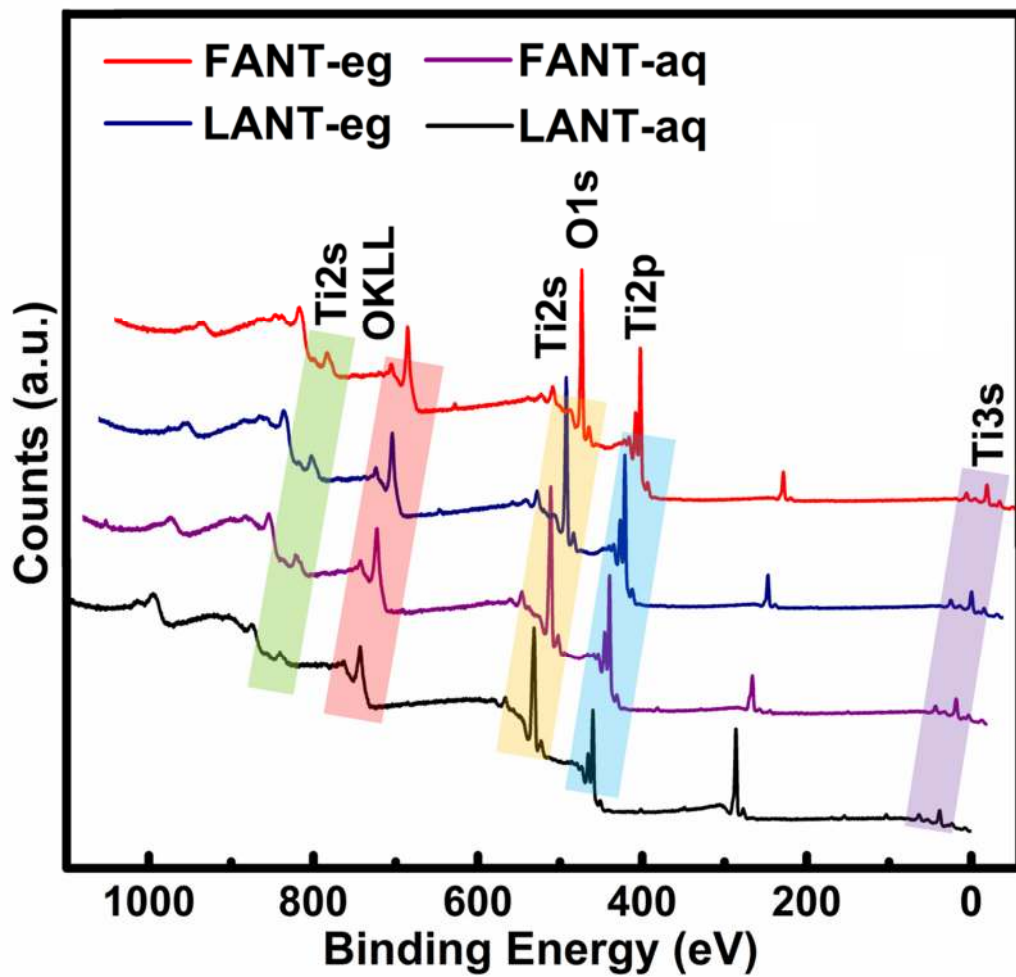


Figure S5. XPS survey scan of FANT-eg (red), LANT-eg (navy blue), FANT-aq (purple) and LANT-aq (black).

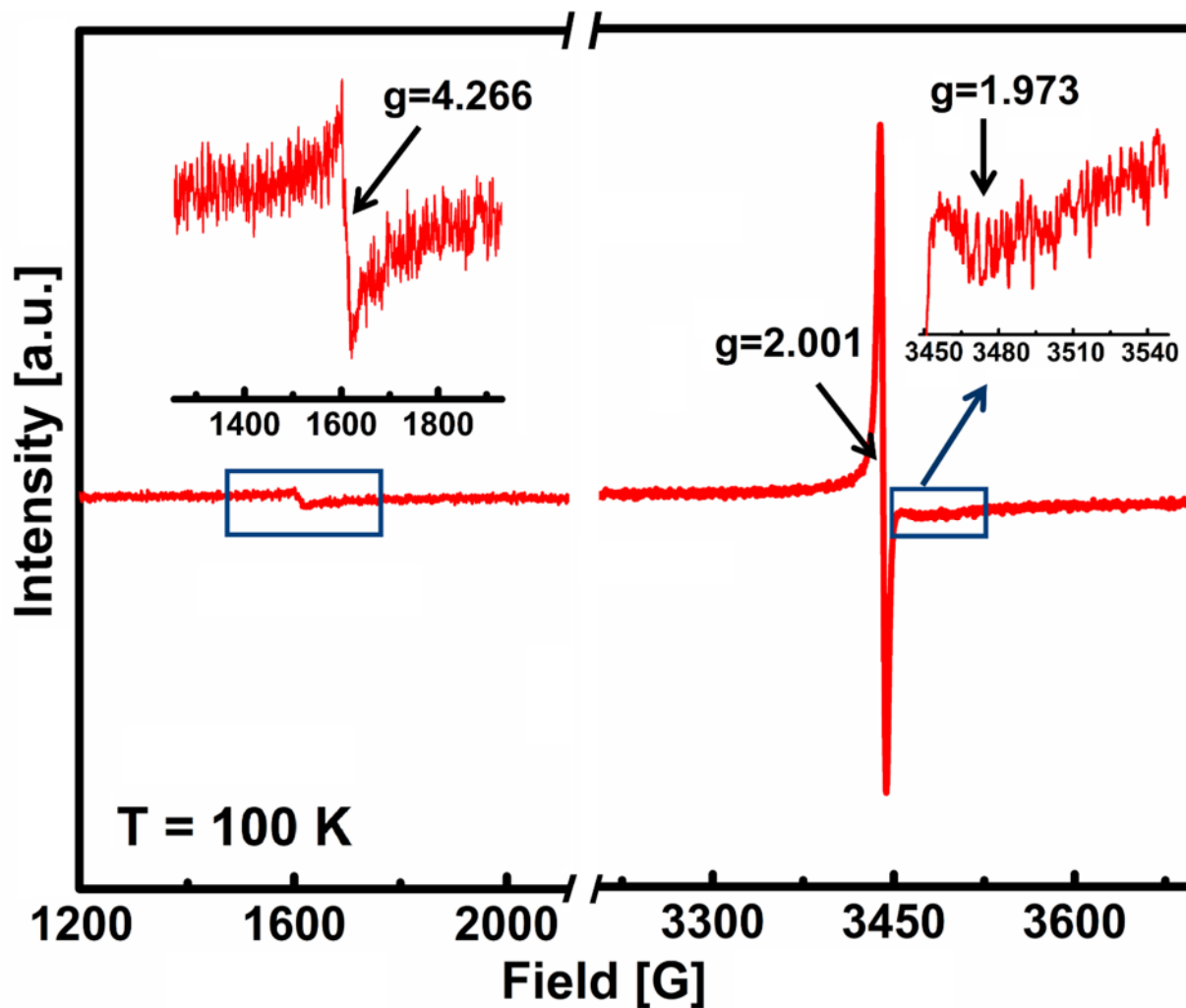


Figure S6. X band EPR spectra of FANT-eg sample recorded at 100 K under dark. The Insets show magnified view of regions and their respective g values. The signal intensity was not optimal (loss of signal occurred) due to the following reasons: (i) The spectra were collected in the presence of O_2 and (ii) At a temperature of 100 K, electrons have enough energy to exchange vacancy site which may lead to pairing of some fraction of unpaired electrons resulting in reduced signal intensity.

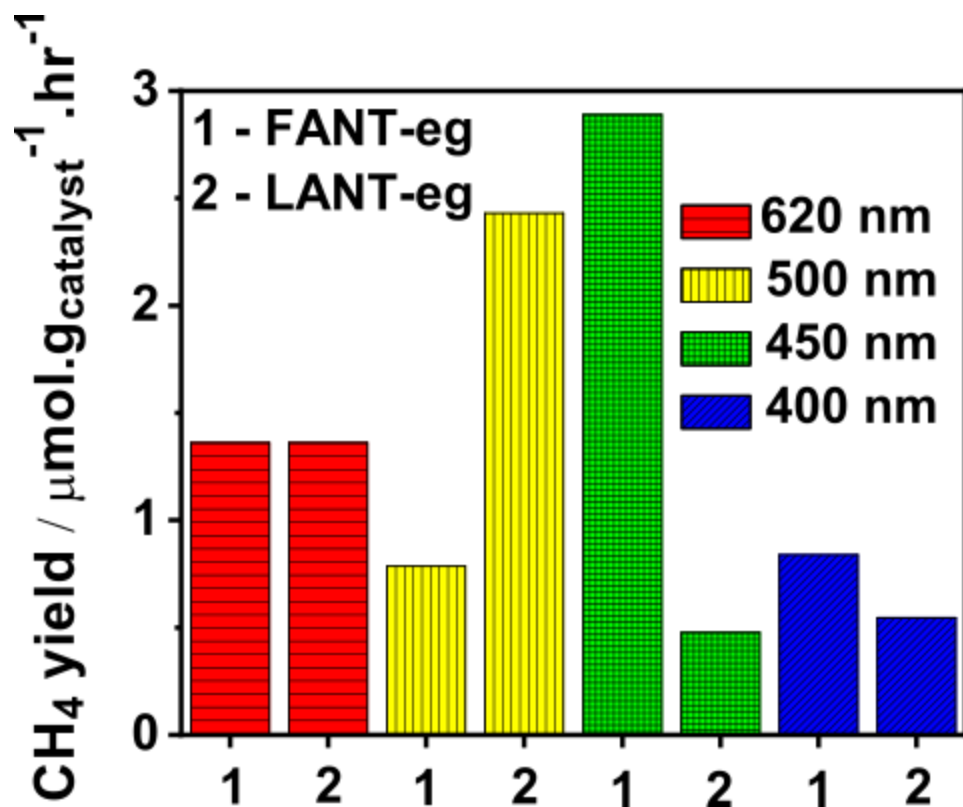


Figure S7. Plots of CH₄ yield (in terms of μmol g catalyst⁻¹.hr⁻¹) for FANT-eg and LANT-eg, using LEDs of different wavelengths (400, 450, 500 and 600 nm). LED lights were operated with a power density of 10 mW cm⁻² and the photocatalytic reactions were performed for 2 hours.

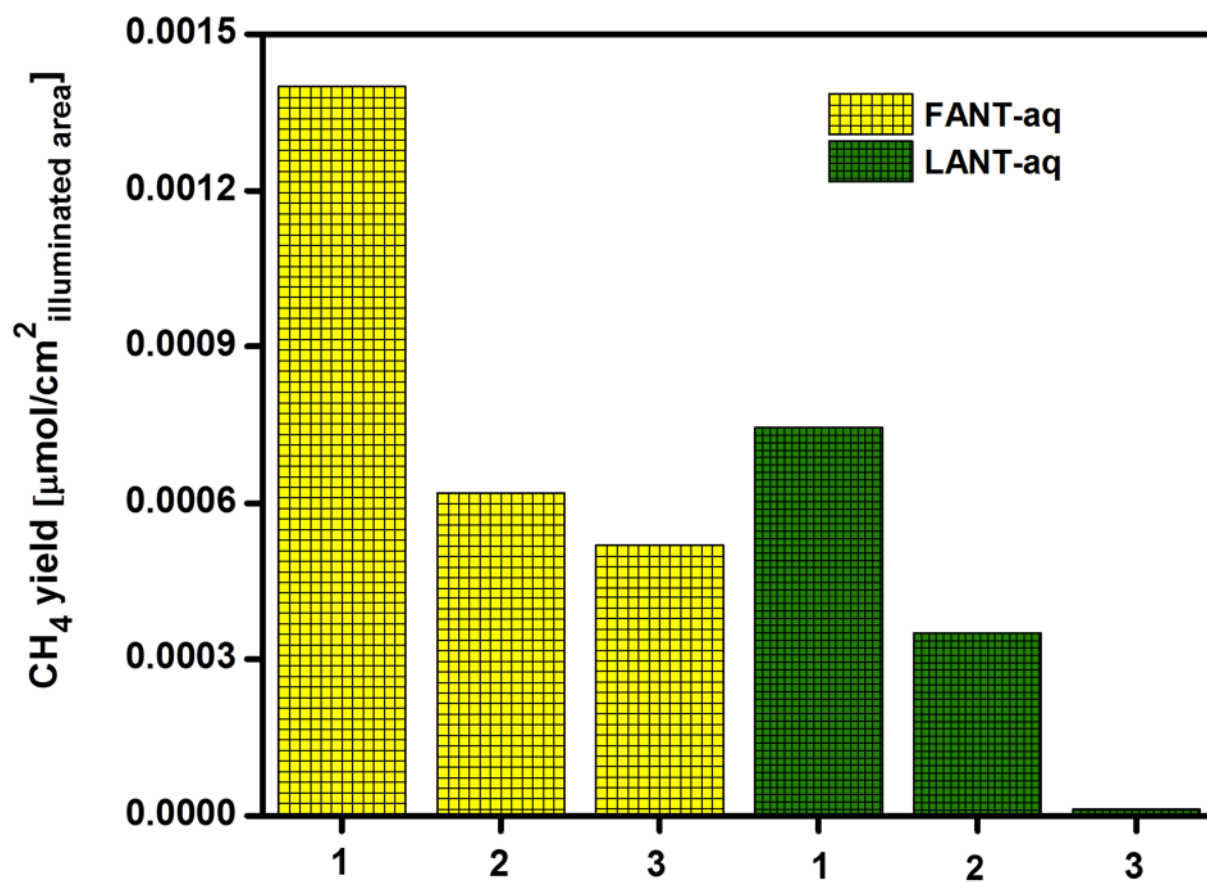


Figure S8. CH₄ yield (in terms of $\mu\text{mol cm}^{-2}_{\text{illuminated area}}$) of CO₂ photoreduction using FANT-aq and LANT-aq under different conditions of illumination. Experiments were performed in presence of water vapor at 80 °C.

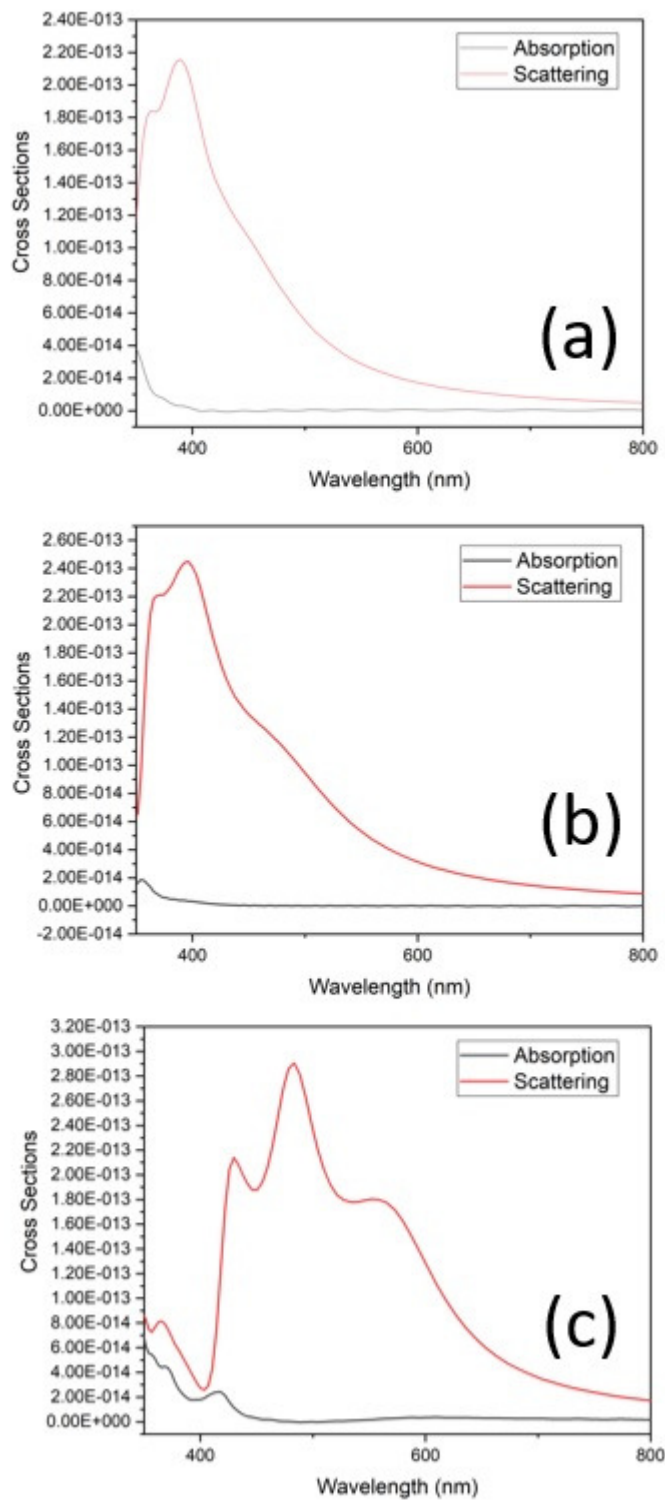


Figure S9. Plots of the absorption and scattering intensity of single nanotubes for (a) LANT (b) FANT-eg and (c) FANT-aq.

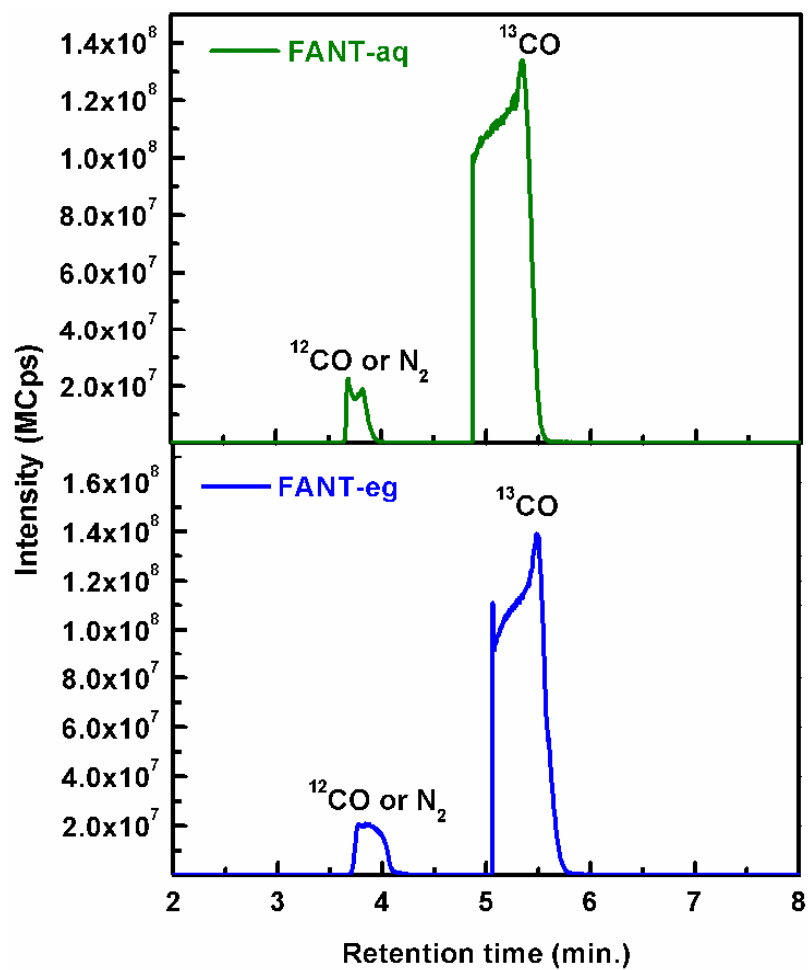


Figure S10. GC-MS chromatogram showing the presence of carbon monoxide in the product gas mixture; CO is a key intermediate in the carbene pathway for CO₂ photoreduction.

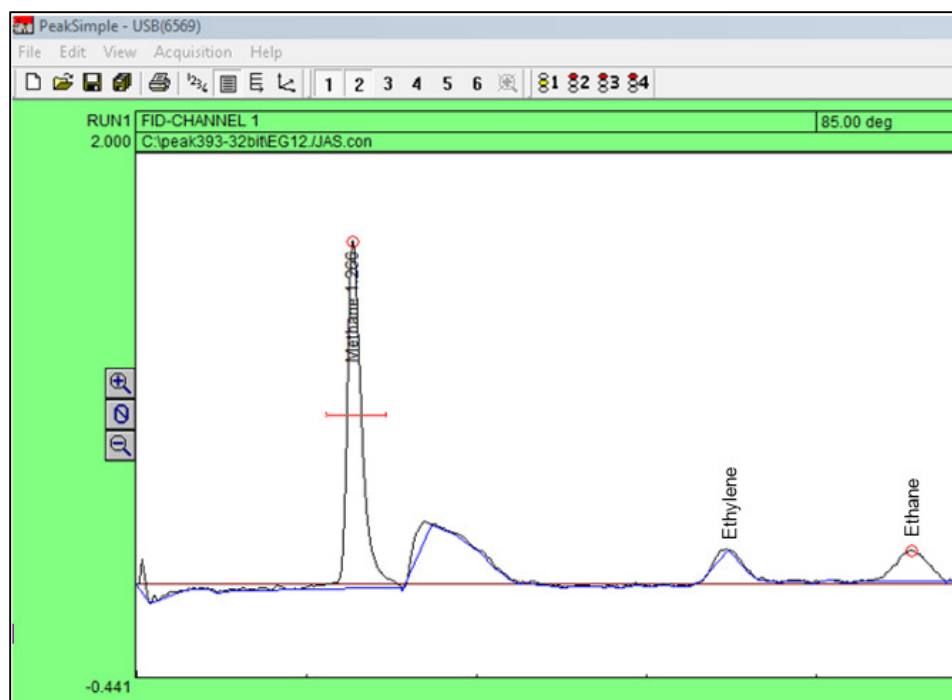


Figure S11. GC-FID chromatogram showing CO₂ reduction products. The feature immediately after the methane peak is due to carbon dioxide and not a flammable product. Ethane and ethylene were in much smaller quantities compared CO and CH₄.

Experimental method for HPLC

For the liquid phase reaction, a 60 mL cylindrical borosil glass vessel ($\phi = 2.5$ cm) was charged with 25 mL DMF and H₂O mixture (1:3) equipped with magnetic stirrer. Subsequently, sample was introduced and the vessel was sealed with the help of a rubber septum. The obtained reaction mixture was purged with N₂ gas for 30 min to remove any other dissolved gases followed by purging with CO₂ for additional 30 min to saturate the solution with CO₂ under dark conditions. DMF and water mixture were used to carry out liquid phase reaction due to excellent solubility of CO₂ in DMF at room temperature which afforded more CO₂ availability during the reaction.¹⁻³ The vessel was then irradiated with 50 W white cold LED light with stirring for 24 h. Following the reaction, the obtained photoreduction product was analyzed with HPLC (Agilent 1100 HPLC with DAD/ESLD, equipped with C18 250×4.6mm, 5 μ m column using acetonitrile: acetone 60:40 mobile phase with a flow rate of 0.5 mL min⁻¹ at wavelength of 205 nm UV detector). The analysis of liquid reaction product did not display the presence of methanol, formic acid and formaldehyde. To validate the absence of any possible reduction product, the reaction mixture was also analyzed

with HPLC equipped with mass spectrometry (Agilent LC/MSD XT) which did not exhibit mass fragments corresponding to any possible reduction product in the formaldehyde pathway.

References

1. J. Chem. Eng. Data, 2012, 57 (4), pp 1249–1266
2. J. Electroanal. Chem., 289 (1990) 203-215
3. Fluid Phase Equilibria 334 (2012) 106–116

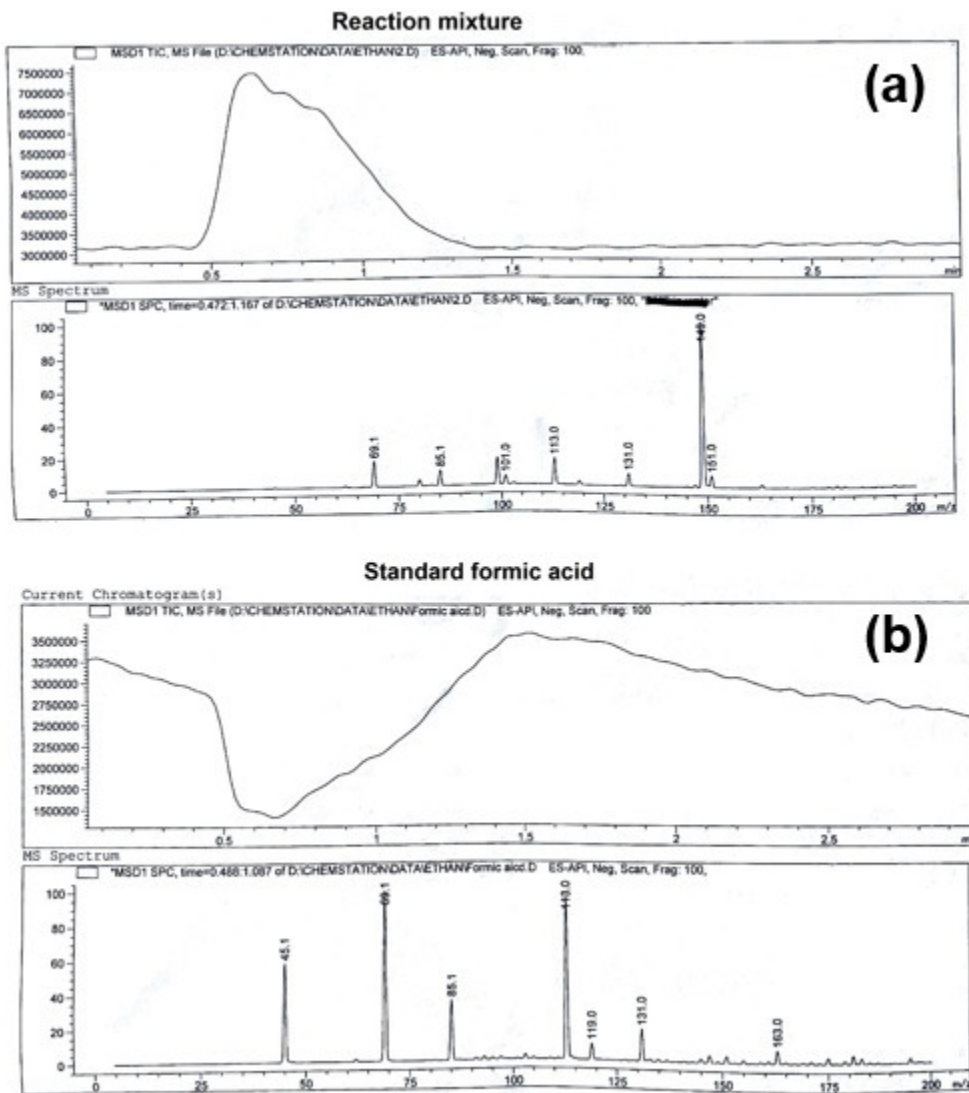


Figure S12. HPLC Mass pack chromatogram of (a) CO₂ photoreaction product and (b) standard HCOOH after 24 hours visible light irradiation using UV detector.

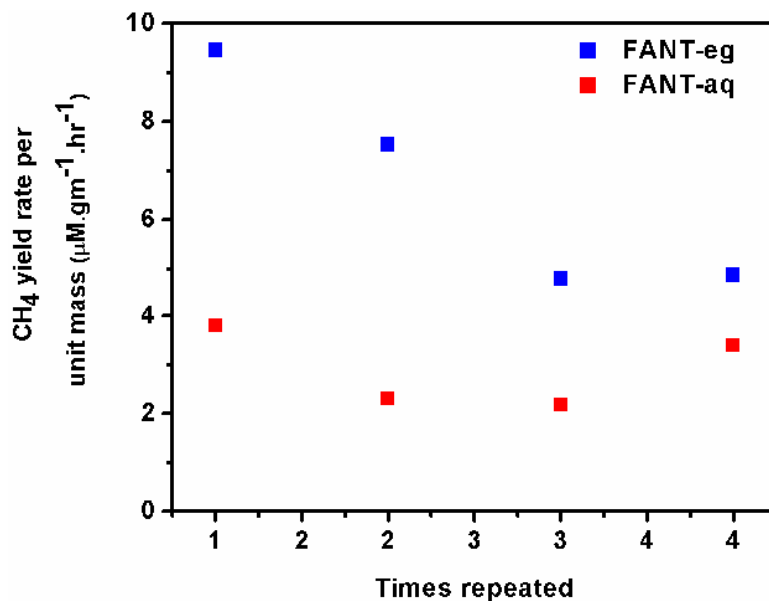
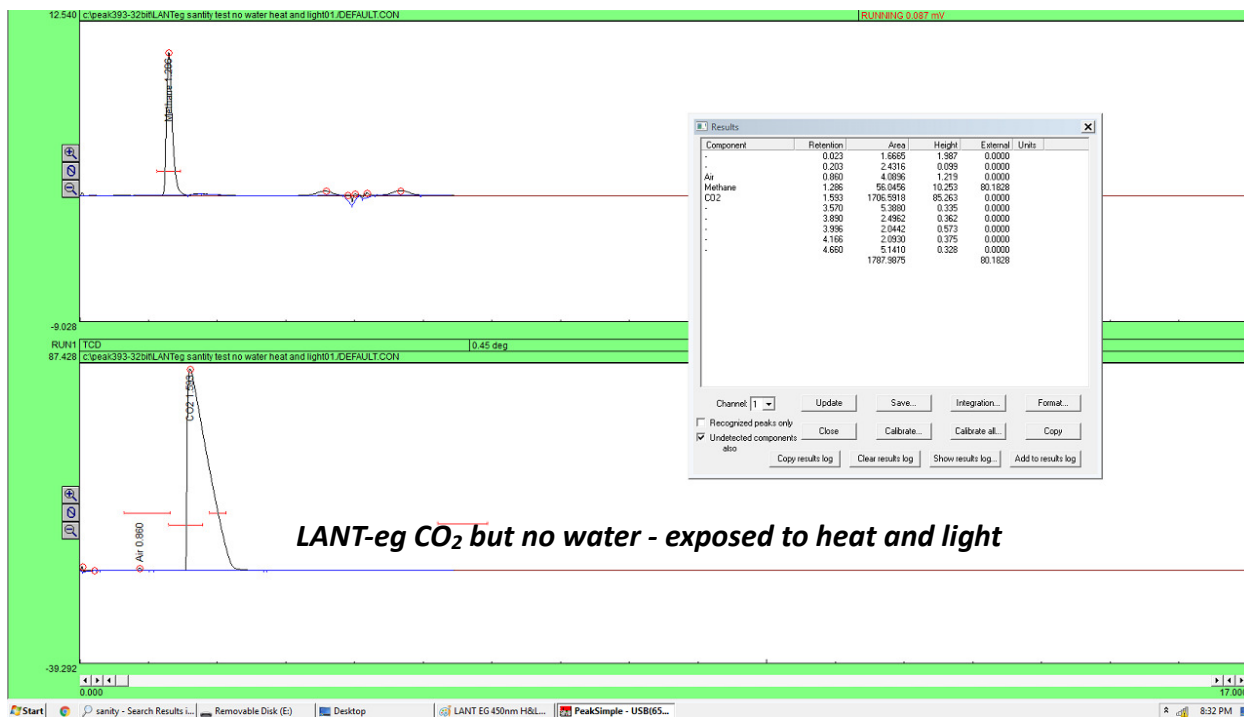
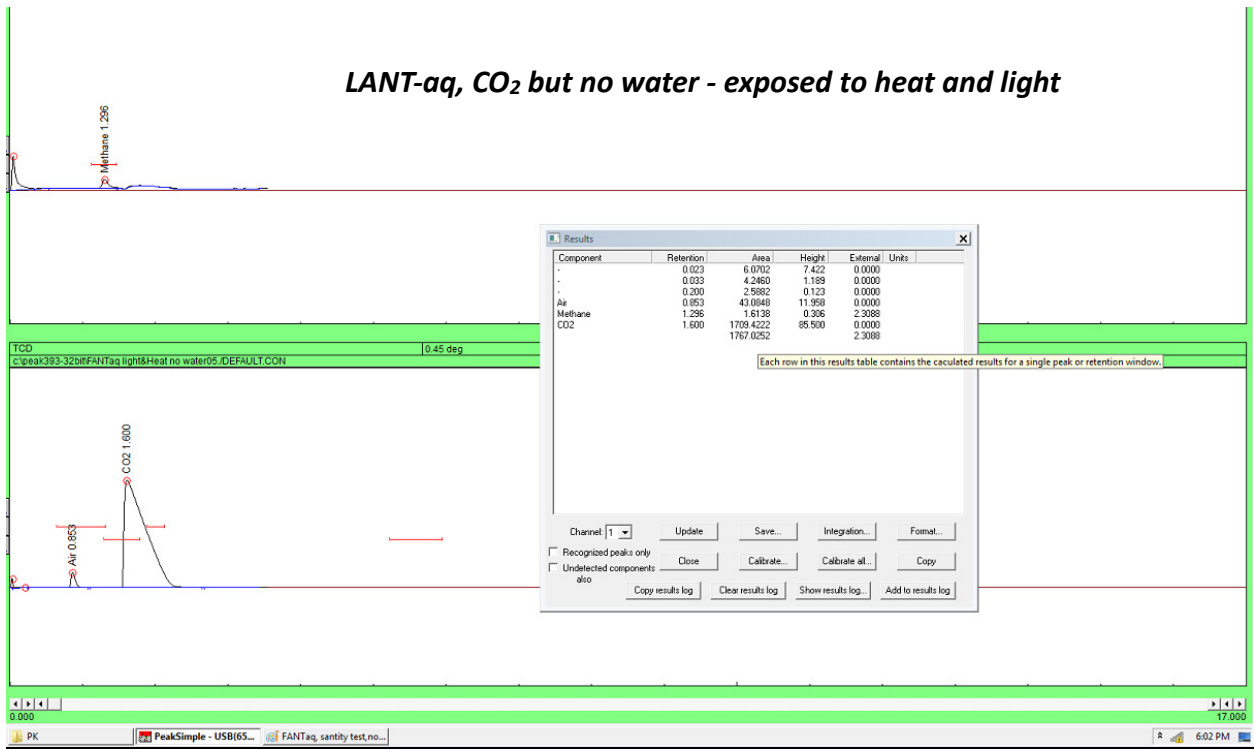
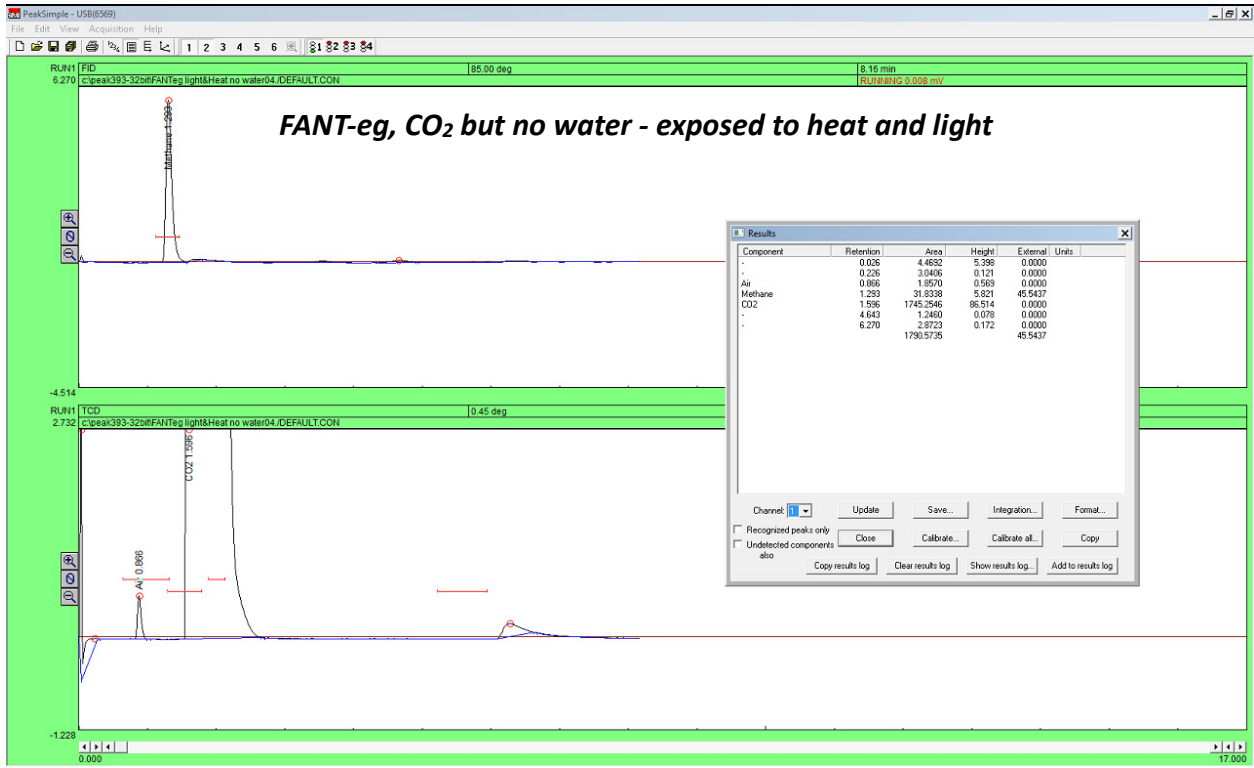
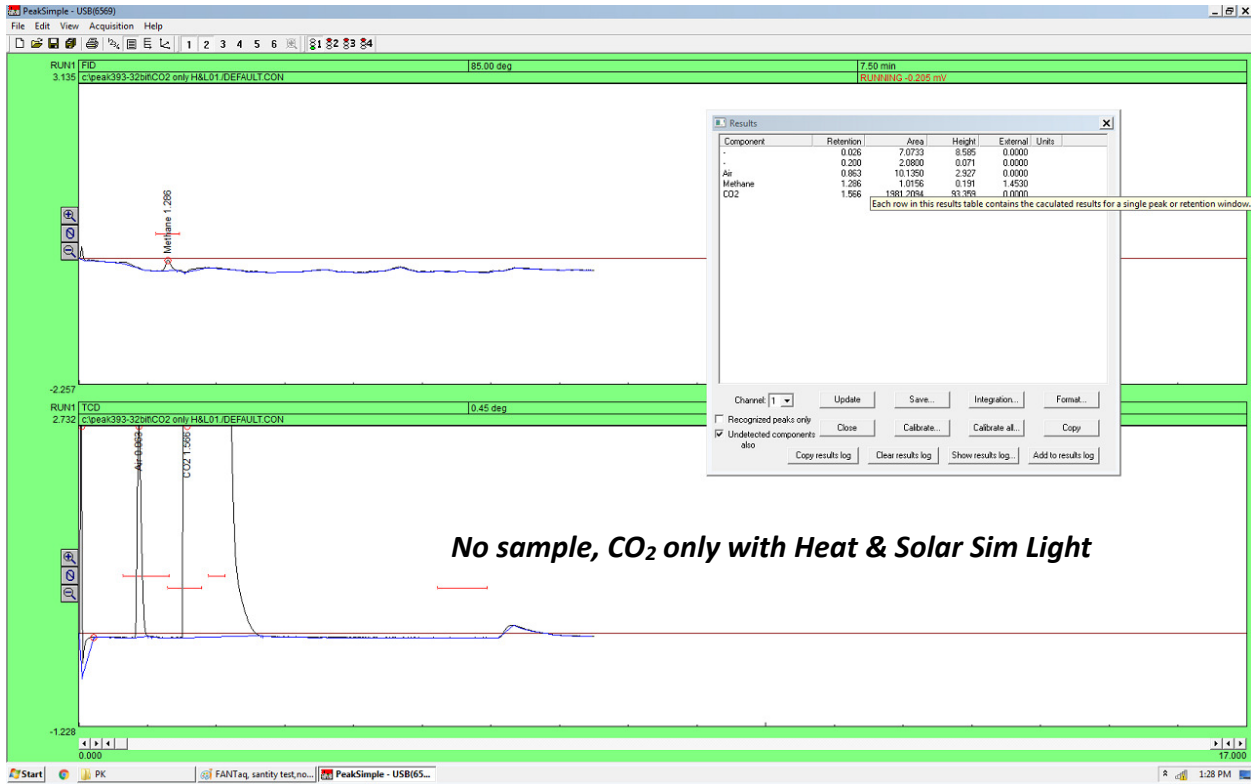
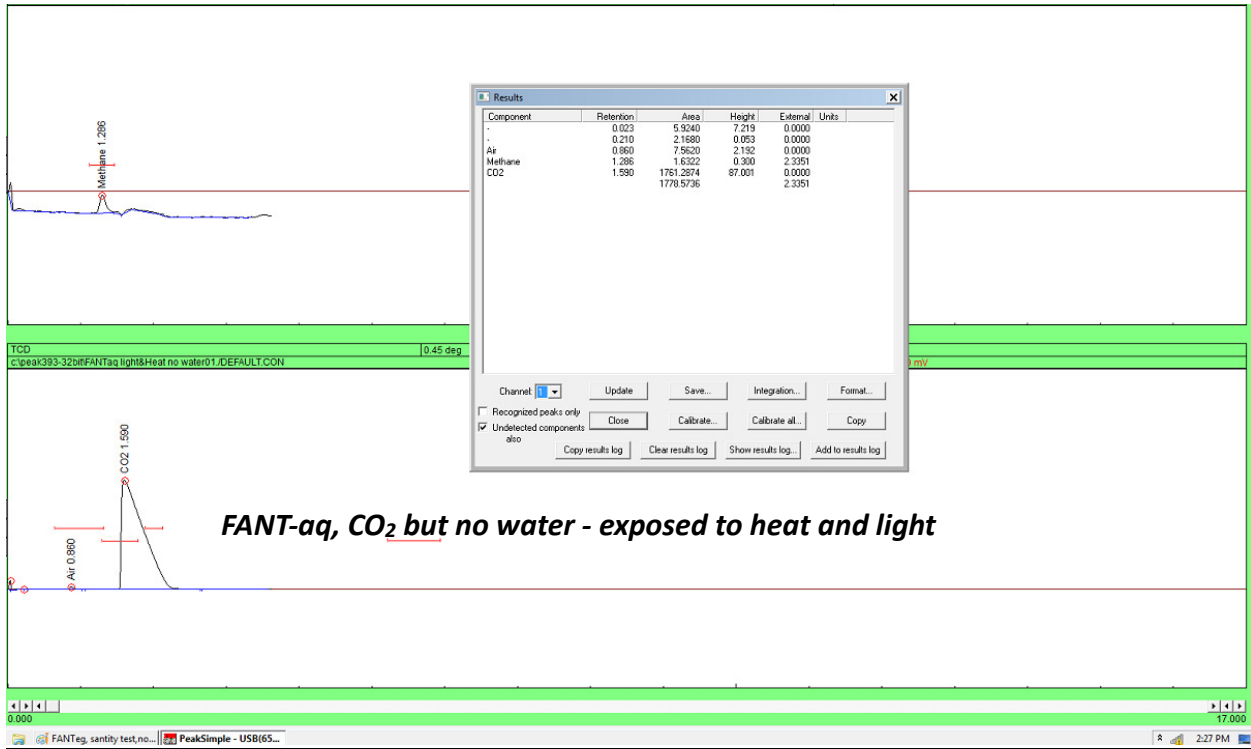


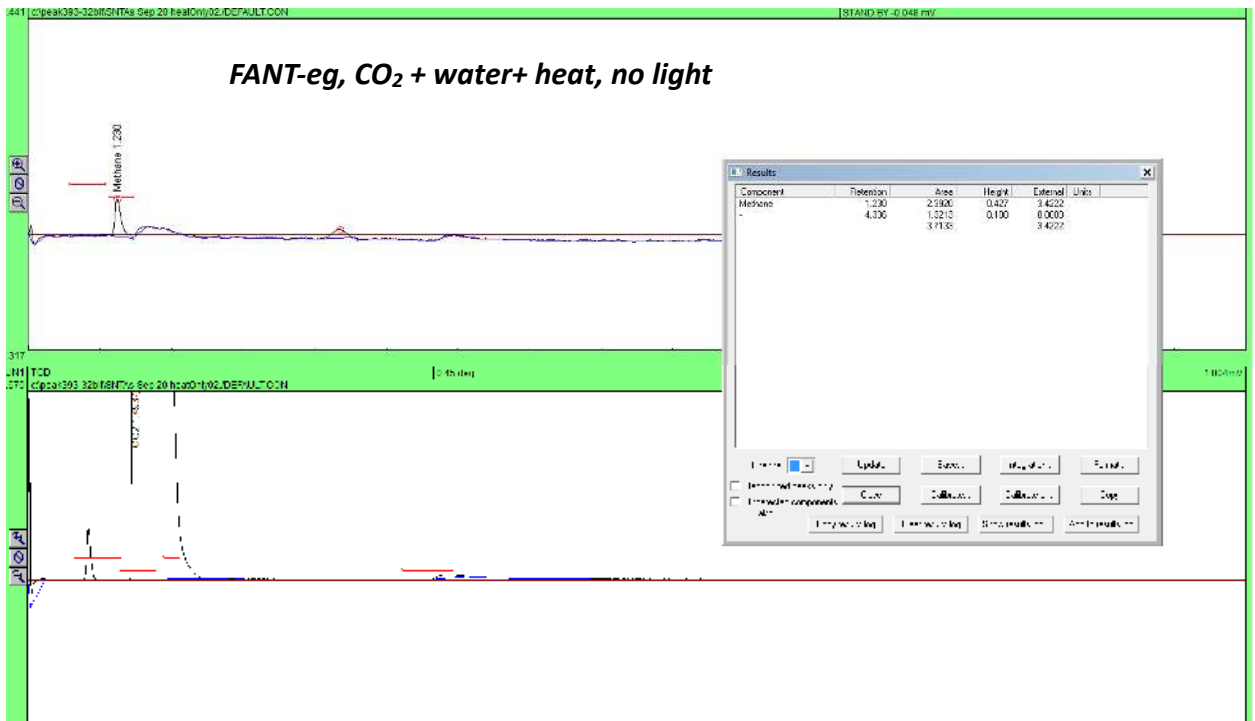
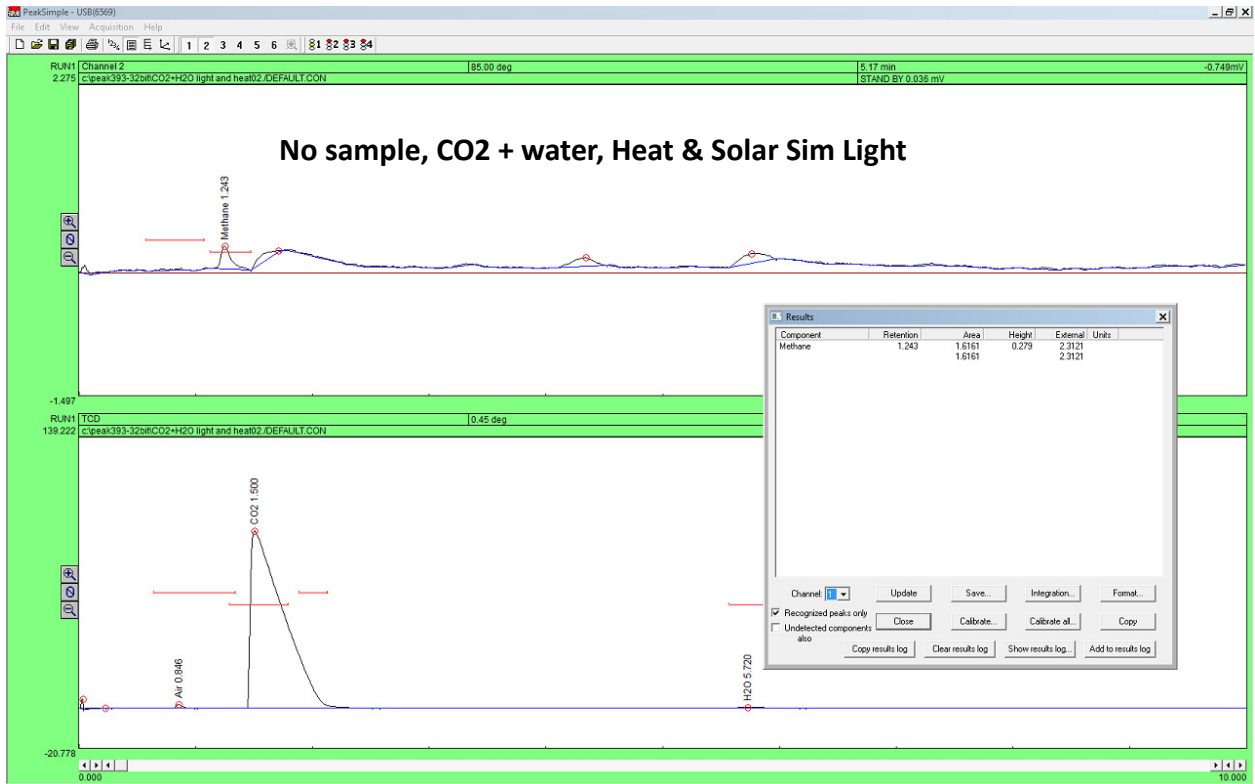
Figure S13. Plots of re-usability test results of FANT-eg and FANT-aq nanotubes. Data was collected in presence of CO₂ and water in the reactor as specified in the experimental setup of the manuscript, and under AM 1.5G, 100 mW.cm⁻² illumination and application of heat at 75 °C.

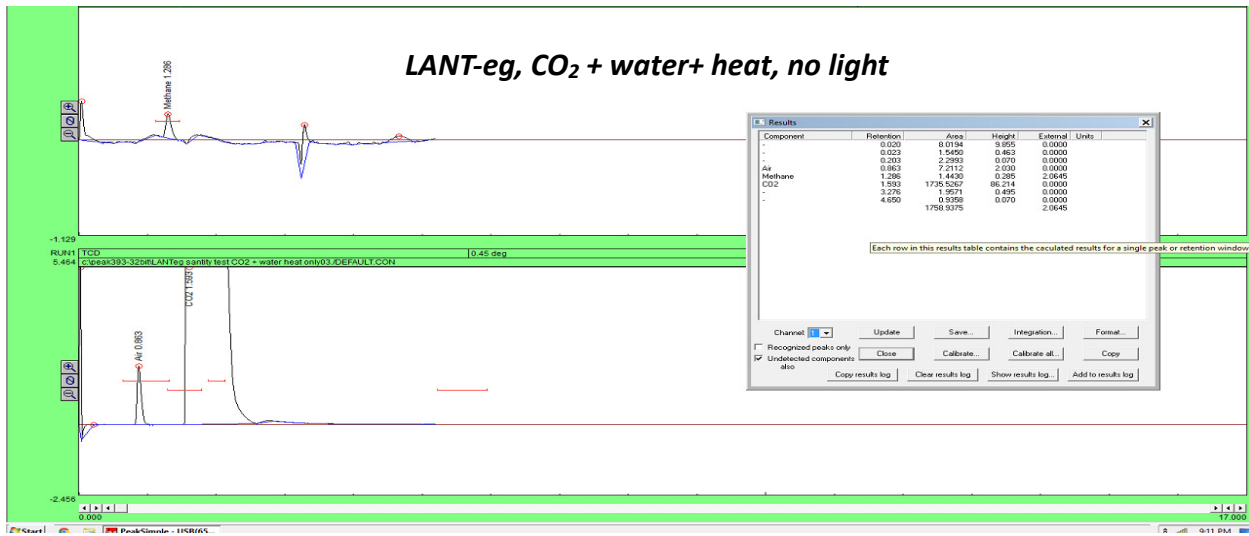
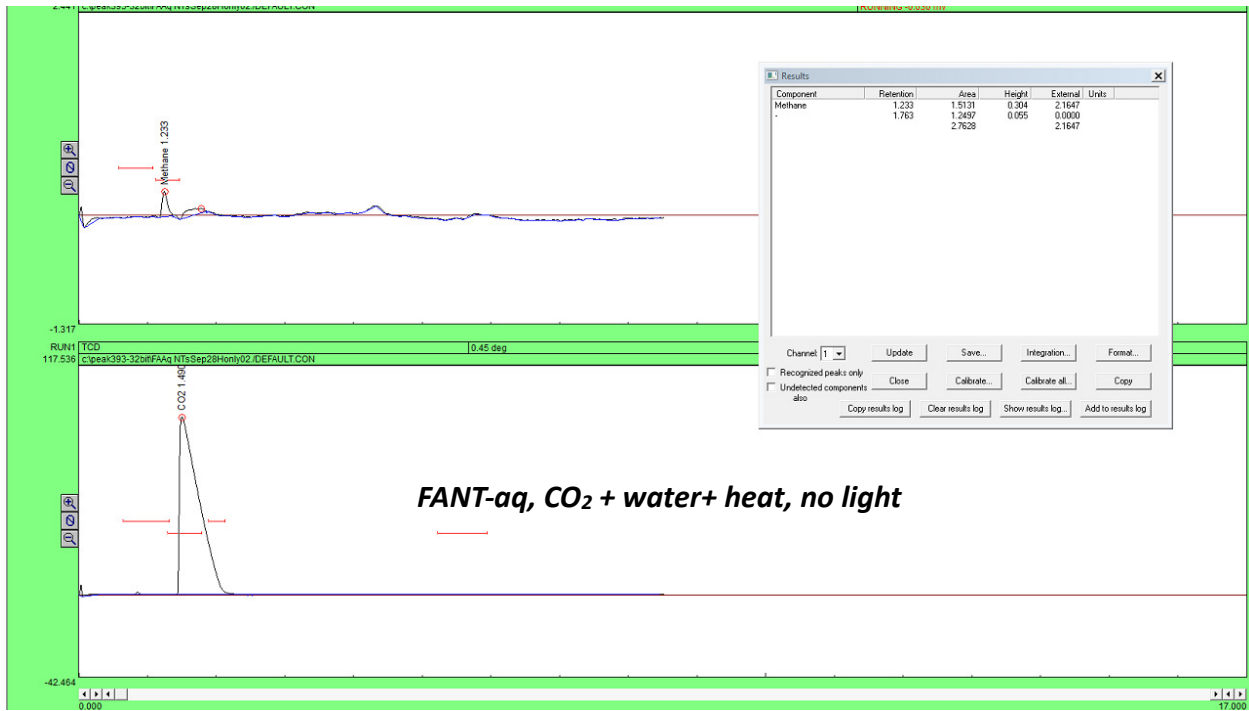
GC TCD + FID Outputs for Various Confirmation Tests

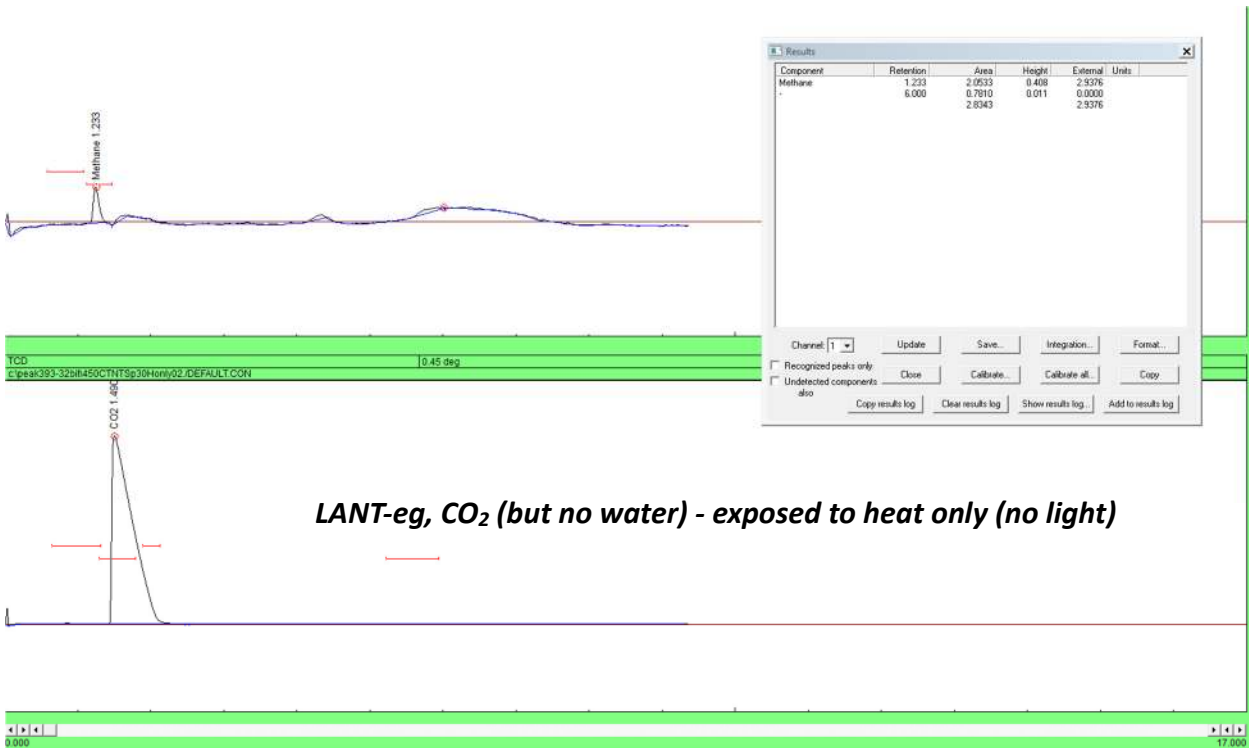
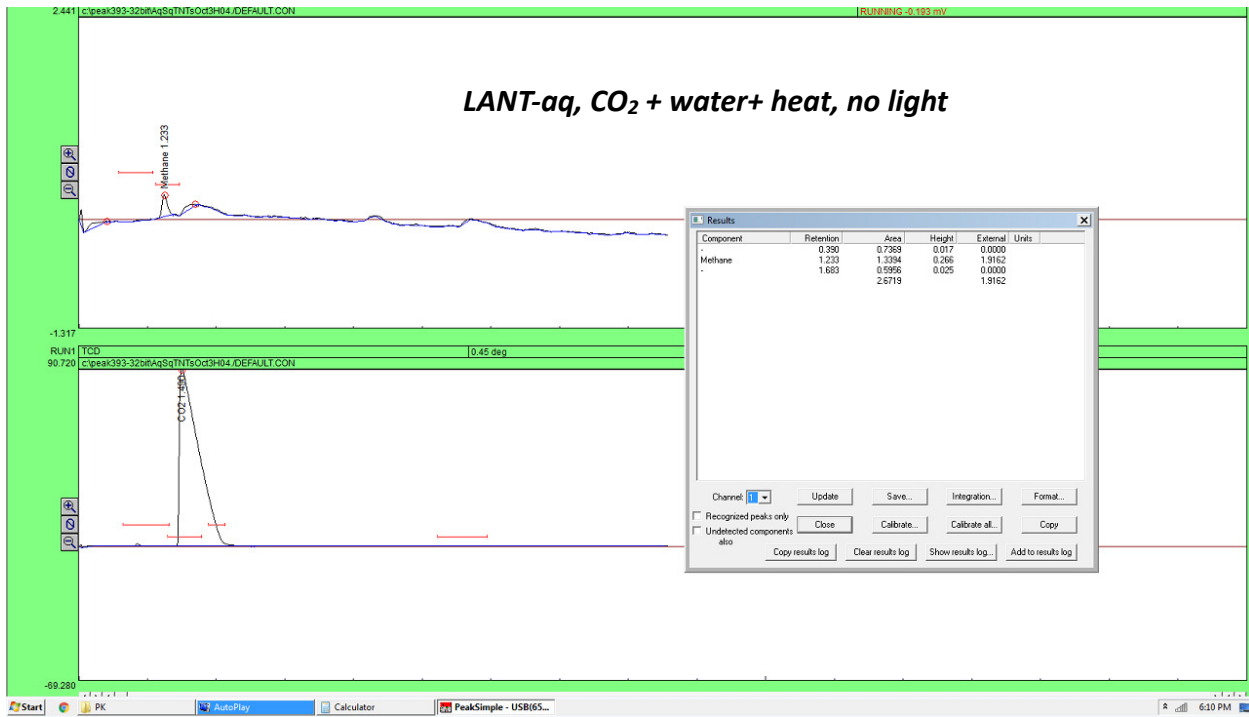


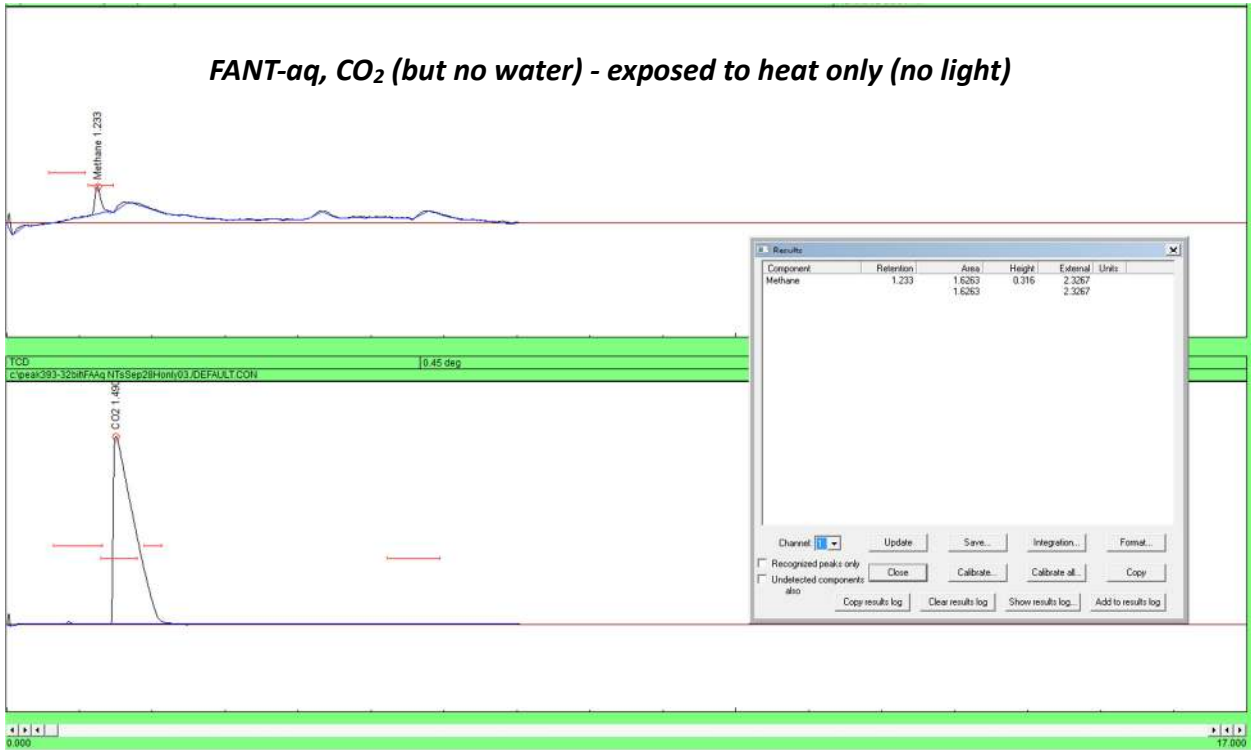
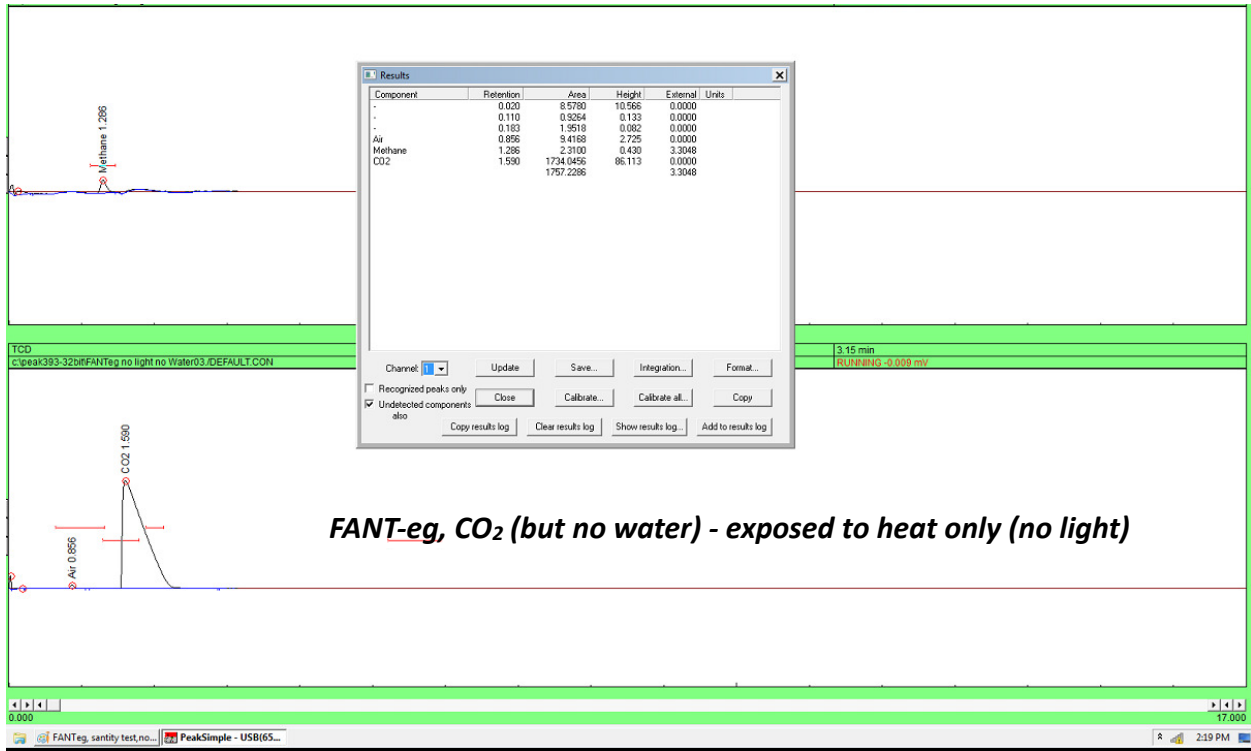








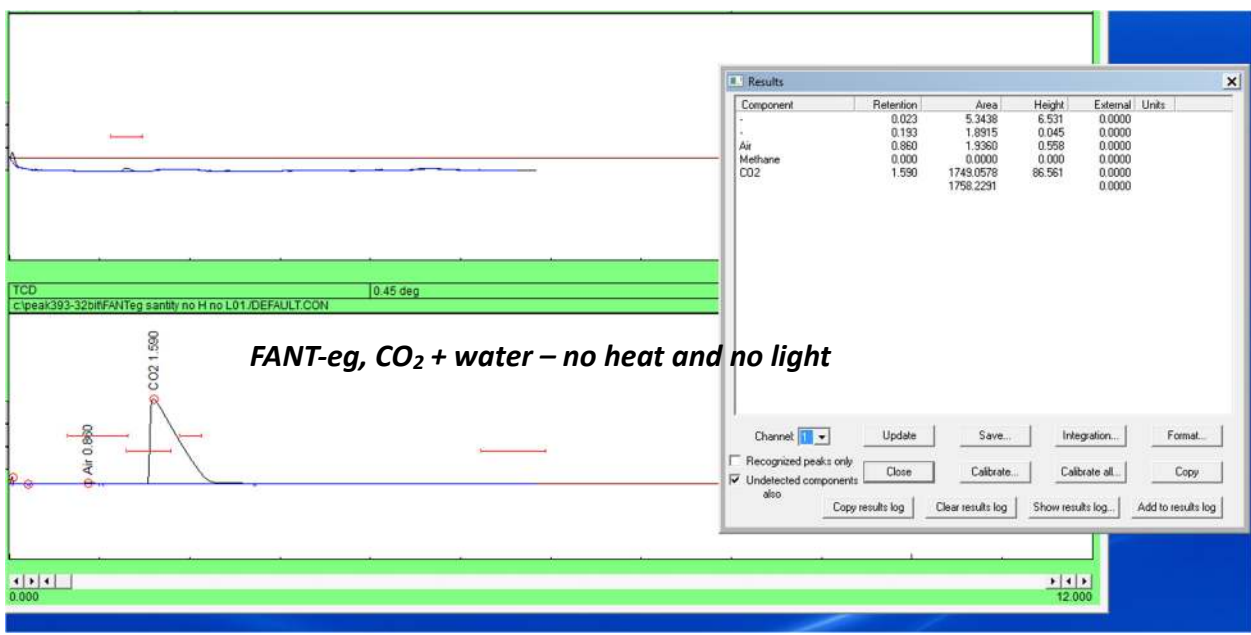


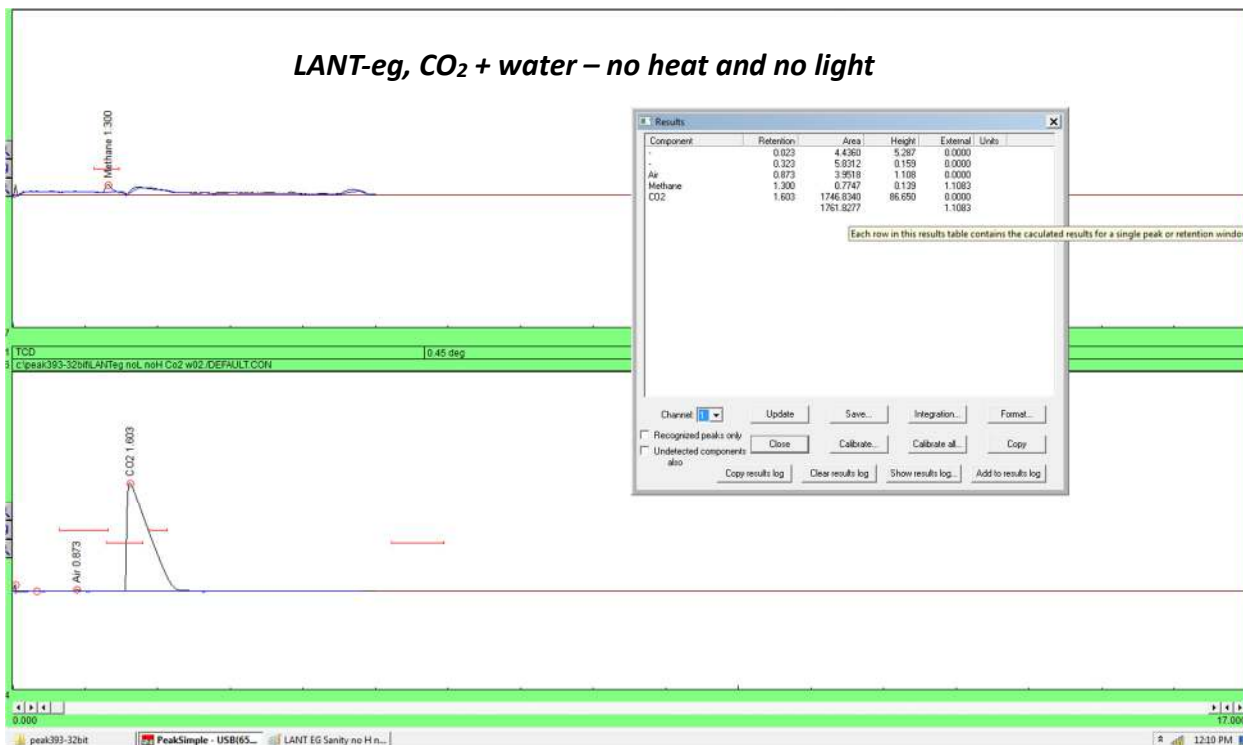
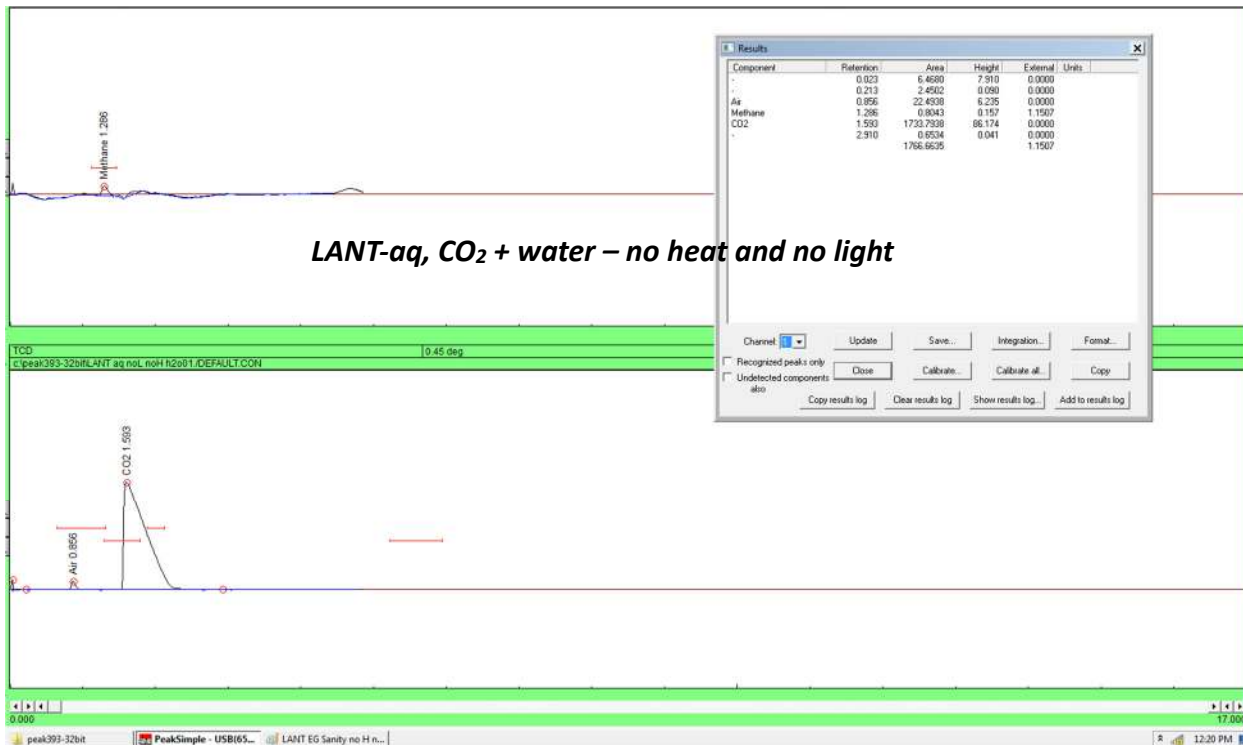


LANT-aq, CO₂ (but no water) - exposed to heat only (no light)



FANT-eg, CO₂ + water – no heat and no light





FANT-aq, CO₂ + water – no heat and no light

